THE KINETICS OF SULPHUR TRANSFER BETWEEN SO_2 AND MOLTEN IRON

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S U M M A R Y

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A study has been made to evaluate some of the kinetic factors affecting sulphur transfer between SO_2 and molten iron. Gas atmospheres containing varying concentrations of SO_2, with or without the addition of CO_2 were passed at 1400°C and 1450°C over molten samples of iron-carbon alloys or iron-carbon-silicon alloys, and the amount of sulphur picked up by the samples was determined.

The effects of change in temperature, sample geometry, the gas sulphur potential, the gas oxygen potential and in the crucible material on the amount of pick up, were noted.

The actual rate of sulphur pick up in each experiment was calculated, and compared with the theoretical sulphur and oxygen fluxes. The actual rate of sulphur pick up was found to have the same magnitude as the theoretical sulphur flux. It appears thus that sulphur diffusion from the surface of the metal to its bulk is the rate controlling step in the transfer of sulphur from gas to metal, which is to be expected in the absence of artificial stirring of the melt. Because of experimental difficulties, the actual rate of carbon loss could not be

accurately determined. An estimated value for carbon loss did have the same magnitude as that of the rate of sulphur pick up.

From the results of this work it appears that there is local equilibrium between the melt and the gas film immediately adjacent to it and that the overall reaction for the sulphur pick up by the metal is

$$SO_2 + 2\underline{C} = 2\,CO + \underline{S}$$

which may be written as

$$SO_2 = \underline{S} + O_2$$
$$O_2 + 2\underline{C} = 2\,CO$$

so that the effect of the carbon content of the metal on $p\,O_2$ and hence on amount of sulphur pick up is of prime importance.

C O N T E N T S

INTRODUCTION

INTRODUCTION

Since man first knew and admired the properties of meteoric iron, it has been one of man's goals, and one of his great achievements, to produce his own iron, by recovering it from the earthy matter, and by shaping it into a usable form. It is hard to imagine what course civilization would have taken, had not mankind developed the methods of iron production.

As man came to know and take advantage of the admirable mechanical and structural properties of iron, he also came to know the harmful effect of sulphur on these mechanical and structural properties. With the advent of modern scientific thought, and technology, the problem of sulphur control in iron and steelmaking processes is one that has been intensively considered.

Up till now, the major economic methods for the production of tonnage iron and steel, are based on the use of carbon, in the form of fossil fuels, as the reducing agent for the recovery of iron from its naturally occurring oxides, , and also as the main source of thermal energy, essential in the chain of operations leading to the production of iron in its final form.

No naturally occurring fossil fuel is known to be sulphur free, and as such the fuel is the main source of contamination of the metal by sulphur.

When the demand for iron and steel was relatively small, and when large deposits of high quality fossil fuels were available, the iron producer could be selective and only the best raw materials were used in iron production. With the advance of civilization, the demands on iron and steel became more exacting. The normal sulphur content, for the ordinary grades of steel, became too high for certain modern uses. In the great demand for iron and steel parts to work under high temperatures, the disastrous effects of sulphur became a grievous problem. At the same time, the high quality raw materials were dwindling and the iron producers have now to use poorer and poorer qualities of raw materials.

While the ore preparation techniques, which are widely used now for the beneficiation of iron ores have proved their worth in increasing the operational efficiency of the blast furnace, however, the decrease in slag volumes resulting from these preparation techniques have added to the problems of sulphur control. Once the sulphur contaminates the liquid metal in the blast furnace, the only possible method of removing it is by its partitioning between the metal and a slag phase chemically able to stabilize sulphur and prevent its return to the metal. Under the conditions prevailing in the blast furnace the transfer of sulphur to the slag phase is quite favourable, the higher the temperature, the more so. It is obvious that for a given chemical

composition of the slag, the larger the slag volume, the larger its capacity for sulphur. Thus smaller slag volumes will result in a lower amount of sulphur removal. As to the favourable effect of temperature on sulphur transfer to slags, this is greatly limited by the type of iron to be produced since the use of higher temperature will encourage the reduction of silicon and its transfer to the metal.

The problem of sulphur contamination in open hearth steel-making is another example of the problems of sulphur control. Here the heating and melting procedure, necessitates the combustion of oil, coke oven gas or producer gas which all contain sulphur, over a charge of iron and fluxes. The iron being not so refractory as the fluxes, melts first, and the main danger of contamination of the metal by sulphur in the gaseous phase, comes at this stage when there is direct contact between the gas phase and the melting metal and the insulating slag blanket has not yet covered the metal. In the refining of steel in the open hearth, the slag is the main vehicle for removing sulphur from the metal. If conditions favour the transfer of sulphur from the furnace gases to the slag, the desulphurizing ability of the slag will be reduced.

The physical chemistry of solution of sulphur in liquid

iron is well known. The literature is full of data on the thermodynamics of sulphur transfer between gas-slag and metal. Surprisingly very little has been done in the examination of the kinetics of this process.

Appreciating the critical importance of sulphur transfer, between a gas phase containing sulphur and a melting iron, this work has been an attempt at the evaluation of some of the kinetic factors affecting the sulphur transfer.

LITERATURE SURVEY

LITERATURE SURVEY

A. SULPHUR IN O. H. FUELS, ITS ROLE IN SULPHUR PICK UP BY THE METAL

During the processes of steel-making, sulphur is undergoing continuous distribution between metal, slag and gas phases. To understand the conditions governing the final sulphur content of the melt, many workers investigated sulphur reactions under iron and steel making conditions. Although most of these investigations have been carried out on slag-metal systems (due to its extreme importance in desulphurisation), the possibility that sulphur may be transferred to and from the slag/metal system by the furnace atmosphere, has long been recognised and studied.

Sulphur is present in the open hearth furnace gases as H_2S, SO_2, COS, SO, SO_3 and S_2. The proportion of various sulphur compounds depends on the degree of combustion of the gases, and to some extent on the temperature. Tahir[1] carried out a calculation of gas composition at different stages of the combustion process for a number of typical open hearth fuels. The calculations show that at high CO/CO_2 ratios (i.e. low pO_2) sulphur is present, mainly as H_2S, CS_2 and S_2. As combustion proceeds, SO_2 becomes the principal sulphur compound. At CO/CO_2 ratios from 1 to 0·01 sulphur is present almost entirely as SO_2. At very high oxygen potentials and especially at low temperatures, SO_3 becomes the main sulphur compound present.

Dahlstom and Aitken[8] estimated that one third of the sulphur content of the gases could be retained in the gas checkers and oxidised and removed by the waste gases during the subsequent reversal. Eisenbecken and Schuls[9] however claimed that 70 per cent of the sulphur content of the gases (containing 90 - 220 grains of sulphur/100 cubic feet) could be retained in the gas checkers and burnt out in the waste. The retention of sulphur was attributed to the formation of CaS and FeS from CaO and FeO previously carried over by the waste gases and deposited over the checkers surface. Schenck[4], from a theoretical consideration of the equilibrium of sulphur containing gases with solid CaO, MgO and FeO, has shown that the conditions prevailing in the gas checker on the ingoing side, i.e. low temperature and high CO/CO_2 ratios, do favour transfer of sulphur from the gas phase to the solid. In practice, the desulphurizing action of the gas checkers may be limited by the amount of available oxides deposited on the checkers and the closeness of approach to equilibrium with the gas phase. In the waste gas period the sulphides are oxidised to sulphates and the loss of sulphur to the stack depends on the decomposition of the sulphate formed, which is favoured by high temperature. It is doubtful if the temperature of the checkers is high enough to decompose $CaSO_4$, so that all sulphur is not removed on the outgoing side, and there will

be a steady accumulation of sulphur in the checkers as the furnace operation proceeds.

Whiteley[5] states that solid steel exposed to unburnt gases formed a scale containing as much as 1% sulphur, whereas a slight loss could occur in burnt gases. He has also shown that silica in the scale tends to prevent sulphur pick up, and he has suggested that pig iron is less susceptible to pick up than scrap, presumably because of the formation of a protective siliceous skin and because carbon and Si increase the activity coefficient of sulphur. Preece and Riley[6] summarised their results obtained in an examination of the scaling property of steels at 1100°C as follows.

The composition of furnace atmosphere, especially with regard to its SO_2 and O_2 contents, is an important factor in controlling the scaling properties of steel exposed to it. Sulphur pick up will not occur in furnace atmosphere containing more than 4% O_2.

Herty and coworkers[7] stated that the sulphur content of droplets formed from scrap during melt down is proportional to the SO_2 content of the furnace gases. Nordone, Grove and Nelson[8] indicated that the melt down sulphur depended on the sulphur content of the gases used during charging and melting and, according to them, the sulphur content of the initial charge appeared to be of little importance.

They also stated that the sulphur pick up is independent of the degree of combustion of fuels, provided that the gas is sufficiently oxidising to cause saturation of the iron with oxygen. This could mean that sulphur is picked up at pO_2 in equilibrium with oxygen saturated iron.

Short and Meyrick[9] claimed that the sulphur content of the gases has very little effect on the final sulphur content of steel. They stated that by using a sulphur free gas the gas will pick up sulphur from the melt and deposit it on the checker, so that when the furnace is reversed the sulphur could be picked up again by the gas.

Carter and Tebbs[10] summed up the views of Herty and Co-workers, Jung, Diehl, Dahlstrom and Alwen, Eisenstecken and Schultz, on the role of the sulphur content of the gases on the sulphur content of the bath.

1. The most critical period in the operation of the O.H. for sulphur pick up from the gases is the melting down period, especially if light scrap constitutes most of the charge.

2. The amount of sulphur transferred from gas to metal is proportional to the sulphur content of the furnace gases.

3. If low sulphur or sulphur free fuel is used desulphurization of the scrap may occur. This depends on relative sulphur content of scrap and gas.

4. For a given sulphur content of the gas, the most important factor affecting sulphur absorption from the furnace gases by the melting iron is the state of combustion of the fuel. In all cases, sulphur will be adsorped from furnace gases containing sulphur, when combustion is incomplete, although sulphur may be lost to furnace gases when combustion is complete.

5. The best way of minimizing sulphur pick up, apart from using a low sulphur fuel, is to shorten the melting down period to a minimum by using a hot flame.

Carter and Tahir[10] observed however that most of the above statements are qualitative in nature.

B. REACTIONS OF SULPHUR WITH MOLTEN IRON

The thermodynamic properties of dilute solutions of sulphur in iron are well known. The solubility of sulphur in liquid iron is so high, that if reducing gases containing sulphur come in contact with molten iron, all the sulphur should be absorped. However, in practice the contact between the sulphur containing gases and the molten metal is poor, due to the presence of the slag layer, and low concentrations of sulphur are usually met. (Barnshaw[11] showed that for $FeO-SiO_2$ slags the slag layer is not a barrier to sulphur pick up).

The standard free energy of solution of gaseous sulphur in liquid iron was given by Sherman, Alexander and Chipman[45]

$$S_2 = 2\underline{S} \qquad \Delta G^\circ = -63,040 + 10{\cdot}54\,T \quad \ldots\ldots(1)$$

The thermodynamic properties of solutions of sulphur in liquid iron were determined mainly from the study of the reaction

$$H_2(g) + \underline{S} = H_2S(g) \qquad K_2 = \frac{p\,H_2S}{pH_2 \cdot a\underline{S}} \quad \ldots\ldots\ldots(2)$$

Maurer and Bischof[40] carried out an investigation for the determination of the equilibrium constant for this reaction. However, due to refractory trouble, the reaction did not reach equilibrium, and the equilibrium constant given $K_2 = \frac{pH_2S}{pH_2\,\%S}$ was only an estimated one. They did however find a linear relationship between the $\frac{pH_2}{pH_2S}$ ratio and the sulphur content of the metal.

Chipman and Tait[44] used an induction furnace in the study of this reaction and carried out investigations in a temperature range of 1513° - 1640°C. Melts containing 0·3 - 1·3% S were studied. A preheated mixture of H_2S and H_2 was passed over the surface of a small pool of metal maintained at constant temperature. The metal was cooled rapidly and analysed. The advantages of using an induction furnace giving a good stirring effect are offset by the steep temperature gradient in the system promoting thermal diffusion. Here the difference in densities of H_2S and H_2 resulted in that the

gases near the hot surface became richer in the lighter gas - hydrogen. The value given by Chipman and Fa Li for the equilibrium constant K_3 was 0·00199 at 1600°C. This value was a $\frac{1}{100}$ fraction of that of Maurer and Bischof. This difference in the K_3 values was attributed to the fact that Maurer and Bischof had used beryllia crucibles in their investigations. Chipman and Fa Li found that BeO crucibles picked up sulphur from H_2/H_2S gas mixture. White and Skelly[16] used a resistance wound furnace in investigating the reaction in the temperature range 1555 - 1600°C. The reaction chamber was small enough to be entirely in the hot zone of the furnace. Small iron beads weighing about one gram were placed on an alumina tray in the reaction chamber. By taking the average values of the ingoing and outgoing H_2S/H_2 ratio, and by taking the 3 runs giving the lowest value, these writers gave an equilibrium constant K_3 of 0·0025 at 1600°C. However the narrow temperature range investigated and the high silicon content of the metal, which was as much as 2·6 per cent Si, leave the K_3 value given in some doubt.

Morris and Williams[16] established the effect of increasing the silicon content of the metal on the amount of sulphur absorped from H_2S/H_2 gas mixtures. They determined the K value for a pure Fe-S system at 1615°C to be 0·00256.

Sherman Elvander and Chipman[28] investigated the effect of S concentration on the activity coefficient of sulphur. The solutions of sulphur in liquid iron were found to deviate from Henrian behaviour at 3% above 0·5 wt % and $e_S^S = \frac{\log f_S}{wt\ \%\ S} = -0{\cdot}03$ so that increase in sulphur concentration decreases the activity of sulphur in the melt. They found that the equilibrium ratio $K = \frac{pH_2S}{pH_2 \cdot \%S}$ at different sulphur concentrations up to 4% not to be a true constant. The true value would be obtained by the graphical extrapolation to zero sulphur. These workers stated that their K_S value was in good agreement with the results of Morris and Williams[16] and with the corrected values of White and Skelly[15].

The influence of alloying elements on the activity coefficient of sulphur was determined by several workers. Morris[17] found that manganese decreased the activity coefficient of sulphur in molten iron.

Kitchner, Bockris and Liberman[18] reporting on a study of the effect of C on the activity coefficient of sulphur, stated that saturation of the melt with carbon doubles α_S^S at 1660°C. Morris and Buehl[19] however gave the increase in α_S^S as a sixfold one. They found that silicon has a similar but a smaller effect than carbon.

Sherman and Chipman[20] in a comprehensive study of the influence of alloying elements on the activity of S, stated that

this effect is linear at low concentration of alloying elements and is described by $\log f_S^X = e_S^X$ [wt % X]. It was found that phosphorus, aluminium, silicon and carbon increased the activity of sulphur, while nickel, copper and manganese, which tend to form sulphides, decreases the activity of sulphur. These workers gave a method for determination of the activity coefficient in a multicomponent system in which

$$f_S = f_S^{Fe} \cdot f_S^C \cdot f_S^{Si} \quad \ldots\ldots\ldots\ldots\ldots$$

$$\text{or } \log f_S = \log f_S^{Fe} + \log f_S^C + \log f_S^{Si}$$

They also gave an alternative graphical method for computing the overall activity coefficient. This method was based on an observation of Morris and Buehl.

Little work has been done on the reaction of SO_2 with molten iron, although under the open hearth conditions, the reactions of SO_2 with liquid iron assume great importance.

Maurer and Bischof[18] studied the reaction

$$Fe + SO_2 = FeS + O_2 \quad \ldots\ldots\ldots\ldots\ldots\ldots(3)$$

Their results indicated that the final sulphur content of the metal is proportional to the $\frac{pSO_2}{pO_2}$ ratio. If the above reaction is the controlling one, it should be possible to reduce S to 0.0005 % Sulphur by passing a gas over it in which $pO_2 = pSO_2$. This is

however incorrect. Chipman and Fa Li [16] therefore suggested that since the oxygen formed in this reaction would be absorped immediately by molten iron to form iron oxide then the effective reaction between SO_2 and liquid iron should be

$$3Fe + SO_2 = \underline{FeS} + 2FeO \quad \ldots\ldots\ldots\ldots \quad (4)$$

The equilibrium constant for this reaction is 0.1×10^{6} at 1600°C, which indicates that SO_2 in contact with molten iron should be almost completely absorped. These authors stated that the function of excess air was to produce a protective oxide film which prevents the reaction from going to completion.

The pick up of sulphur from atmospheres containing SO_2 has been studied by Carter and Tehir [10], who passed a mixture of nitrogen containing small percentage of SO_2 over molten iron contained in magnesite crucibles and heated by induction heating. Considerable oxidation of iron occurred which eventually led to the separation of an oxide rich phase. The stirring used by the induction heating caused the slag formed to move to the periphery of the crucible so that the metal appeared to be in direct contact with the gas phase throughout the experiment. The system was far from equilibrium and the $\underline{S}$ values finally obtained were the result of attainment of steady state conditions, in which the rate at which sulphur entered the metal from the gas phase, equalled the rate at which the sulphur entered the continuously forming slag phase from

the metal. The sulphur concentrations obtained were proportional to the pSO_2 in the gas and were greatest at low temperatures. This relationship was expressed as follows

$$\log \frac{[\%\ S]}{pSO_2} = \frac{2642}{T} + 0.350$$

Sulphur vapour was found in the exit gases, so that the reaction was thought to occur in two stages

$$2\ Fe + SO_2 = 2\ FeO + \tfrac{1}{2}S_2 \quad \ldots\ldots\ldots\ldots\ldots \quad (5)$$

$$Fe + \tfrac{1}{2}S_2 = FeS \quad \ldots\ldots\ldots\ldots\ldots \quad (6)$$

followed by separation of an FeO rich slag, when saturation was reached.

By using starting material containing more sulphur than corresponding to steady state conditions, the sulphur content fell, but it was obvious that the rate of sulphur removal was much slower than the rate of absorption because excess S could only be removed through FeO slag whose formation is limited by the amount of O_2 in SO_2. The magnitude of pick up was unaffected by the presence of 1.6% O_2 in the gas mixture, and the authors suggested that their results could be applied to the melting down period provided that the O_2 was high enough to form FeO.

Earnshaw[11] carried out investigations comprising the study of the reactions of SO_2 with liquid iron. This author stated that the rate of absorption of sulphur by molten iron from

a SO_2/nitrogen gas mix was very dependent on the mode of contact of gas and metal phases. Bubbling the gas through the metal increased the contact area of the two phases and hence increased the rate of absorption by the metal. Raising the partial pressure of SO_2 in the gas phase at a constant nitrogen flow increased the rate of pick up of sulphur by the metal but not proportionally. Increase of concentration of carbon and silicon in metal and increase in temperature were found to decrease the rate of absorption of sulphur. This author indicated that it is obvious that absorption of sulphur by molten Fe-C alloys from the gas, could not take place without a simultaneous absorption of oxygen by the metal and hence the removal of carbon. It was very noticeable that the change in the rate of carbon removal was almost proportional to the change in the rate of sulphur absorption. It was found that molten Armco iron absorped sulphur and oxygen from SO_2/N_2 mixtures, the oxygen eventually forming a separate oxide phase which reacted with the gas, and into which sulphur partitioned from the metal. No equilibrium concentrations were found, the rate of absorption being almost uniform throughout, with a slight decrease in the rate at higher concentrations of sulphur in the metal. (Partition of sulphu between slag and melt remained in equilibrium).

It would be constructive to mention here some of the work done on gas/slag relationships which might throw some light

on the gas/metal reactions. Richardson and Withers[21] stated that the transfer of sulphur from slag to gas is accompanied by a simultaneous transfer of oxygen from gas to slag. Similarly, transfer of sulphur from metal to slag is accompanied by a simultaneous transfer of oxygen from slag to metal.

St. Pierre and Chipman[22] examined the equilibrium between gas mixtures of SO_2 with CO or O_2 in which the partial pressures of S_2 and O_2 are known, and lime-iron oxide slags at constant atmospheric conditions. These authors contended that the equilibria between gases and slags could be described by the reactions.

$$O^{--} + \tfrac{1}{2}S_2 \text{ gas} = S^{--} \text{ slag} + \tfrac{1}{2}O_2 \text{ gas} \quad \ldots\ldots\ldots(7)$$

$$O^{--} + \tfrac{1}{2}S_2 \text{ gas} + \tfrac{3}{2}O_2 \text{ gas} = SO_4^{--} \text{ slag} \quad \ldots\ldots\ldots(8)$$

They considered the first to be controlling at oxygen pressures less than about 3×10^{-6} atm., while the second governs the sulphur content at oxygen pressures greater that 3×10^{-6}. Richardson and Pinoham's[23] results fit in with this scheme. At oxygen pressures greater than 10^{-3} to 10^{-4} they found the second reaction was predominant while the first one was controlling at oxygen pressures less than 10^{-5} to 10^{-6}.

St. Pierre and Chipman[35] gave also the free energy of gas reactions comprising sulphur which might occur at steel making temperatures and described the effect of change in the slag composition and of the change in temperature on the sulphur content of the slag.

Rosenqvist and Hymo[36] studied the reaction between iron sulphide and SO_2. They considered it to be

$$3FeS + 2SO_2 = Fe_3O_4 + \frac{5}{2}S_2 \qquad \Delta G^\circ = 23,270 - 1.13\,T \quad \ldots\ldots\ldots(9)$$

The value of ΔG° is valid in 500 - 1000°C temperature range. These authors contended that regardless of which composition the original sulphide has, the sulphur content will adjust itself to be in equilibrium with the gas. If there is an original sulphur excess this will be expelled and may react with any magnetite present to give FeS and SO_2. If there is any sulphur deficiency, sulphur will be picked up from the atmosphere until equilibrium is restored.

Leuing and Richardson[26] examined the thermodynamics of ferrous sulphide and oxide mixtures, and tried a tentative application of their finsings to the open hearth. Assuming that the metal during melting is almost certainly protected by a film of oxide which melts at about 1400°C, they considered that the extent to which sulphur is picked up by the charge is probably governed by the amount of sulphur that this oxide could abstract from the gases

during its formation.

$$FeO + \frac{1}{2}S_2 = FeS + \frac{1}{2}O_2 \qquad \Delta G^{\circ}_{1373-1700} = 25{,}000 - 1{\cdot}54\ T \qquad \ldots\ldots\ldots\ldots\ldots(10)$$

These authors collected samples of oxide drippings in an iron spoon inserted into a 100 ton O.H. furnace, fired with oil containing 1·2% S. By assuming that the Fe_2O_3-FeO ratio in the drippings reflects the CO_2/CO ratio present at the place where the drippings were formed, the sulphur content which would be reached if the drippings came to equilibrium with the gases, could be calculated. The calculations took account of the ingoing steam as well as air and allow for the formation of H_2S, COS, SO and S as well as SO_2. Doing an elaborate calculation in which they took into consideration the effects of temperature, of the degree of combustion of the gases and of the different CO_2/CO ratios over different areas of the flat bath, they estimated that the pick up by the charge is from 20 - 30 lbs, which confirms practical results. Accordingly, they consider it a reasonable working hypothesis that the melting metal is protected by molting oxide and that the absorption of sulphur by this oxide is the most important mechanism of pick up. They also considered that the extent of pick up is mainly determined by the temperature of the oxide and the oxygen and sulphur potential of the gases and that rather less than the equilibrium amounts of sulphur are absorped. They contended that the low oxygen potentials at the Fe/FeO interfaces do not appear to be controlling, otherwise much greater absorption

would probably be found.

Alwan and Mills[80] examined the effect of slags composition on the rate of transfer of sulphur from furnace atmospheres to molten slags. Their experiments were carried out at 1550°C and constant gas composition (CO/CO_2 ratio corresponding roughly to 10^{-8} atmos. of oxygen and 2·8% SO_2 by volume). The only variable was slag composition. These workers found that both the rate and amount of sulphur transfer to slag depended on the state of oxidation of the slag and its silica content, the latter being a very important factor. They represented the replacement of oxygen by sulphur in the slag as

$$(O^{2-}) + \tfrac{1}{2}S_{2gas} = (S^{2-}) + \tfrac{1}{2}O_{2gas} \quad \ldots\ldots\ldots\ldots \quad (11)$$

They considered that at the high temperature used, the rate of the chemical reaction would not be the slowest step and that in the absence of artificial stirring, the slowest step is more likely to be the diffusion of sulphur from the slag/gas interface than the diffusion of oxygen from the melt to the interface. The ionic radius of sulphur being 1·84A° and that of oxygen being 1·4A°. They inferred that the lower rate of sulphur pick up associated with higher silica content must be at least in part due to the decreased rate of sulphur diffusion through the more complex silicate network. Similarly the dependence of sulphur pick up rates by ferruginus slags on their state of oxidation (below a partial pressure of oxygen of 10^{-6} atmos) could be explained on the grounds that ferric iron

is a network former. These authors considered the results of their experiments to be consistent with the theory that sulphur replaced only oxygen which was not bonded to silicon. Higher sulphur concentrations than equilibrium value were obtained.

Ward and Salmon[27] examining the kinetics of sulphur transfer from metal to slag, assumed that sulphur diffusion is rate controlling, and calculating their results on this basis they found out that(

1. The initial transfer of sulphur from metal to slag obeys a first order reaction equation of the form $-\frac{S}{t} = K_M \frac{S}{M}$

2. The rate coefficient K_M is generally increased by

i - increasing temperature

ii - increasing the slag basicity

iii - adding CaF_2 to the slag.

EXPERIMENTAL

PREPARATION AND ANALYSIS OF METAL SAMPLES.

The metal samples in this investigation were mainly iron-carbon alloys with varying carbon contents. In some of the experiments, iron-carbon-silicon alloys were used.

The 4% iron carbon alloy.

Stock Armco iron (C . 0·1 % - Mn . 0·013 % - P . 0·005% - S. 0·035 % - Si . trace), was melted in a graphite crucible using high frequency heating. When the metal was completely molten, it was stirred with a graphite rod, and the hot metal quenched in water. The solid metal, after being cleaned and dried, was broken into small pieces in a percussion mortar.

The 3% and 2% iron carbon alloys.

A calculated mixture of stock Armco iron and of the 4% alloy were melted together in a Morganite crucible using high frequency heating. It was estimated that 25% of the carbon in the alloy was lost during heating and meltingand the charge was made up to compensate for this loss. The carbon content of the alloys was 2·97 % and 2 % respectively as shown by analysis.

The iron-carbon-silicon alloys.

Here a mixture of the 4 % carbon alloy and calculated amounts of ferrosilicon, containing 85 % silicon, were melted together using high frequency heating. It was found difficult to melt this mixture, using a graphite crucible. The iron-carbon alloy was melted first

in a Morganite crucible and lumps of ferrosilicon then added, after the melting of which, the bath was stirred with a silica rod. The alloy was remelted in a graphite crucible, and in this way a homogeneous alloy was obtained. The alloys made contained 0·73 %, 1·83 % and 5·6 % silicon respectively.

Analysis of the metal samples.

(a) Analysis for carbon.

Carbon was estimated both before and after the experiments by the Standard combustion method[20]. Oxygen was passed over alloy millings for 30 minutes at 1100°C, using tin powder as accelerator. The carbon dioxide evolved was absorbed in a "Carbosorb" bulb containing soda asbestos and $CaCl_2$. For the estimation of carbon in samples after the experiments, special care was taken, in putting an additional potassium permanganate gas scrubber in the train, to remove all traces of sulphur gases. Standard iron-carbon alloys were used to check every ten analyses.

(b) Analysis for sulphur.

The estimation of sulphur by the standard combustion method[20] was tried; however, it proved quite untrustworthy and gave erroneous results. For this method to be successful, one has to use standard iron-carbon-sulphur alloys, the sulphur content of which must be comparable to the sulphur content of the analysed alloy. It was

decided to estimate sulphur gravimetrically[88]. Sulphur is converted to potassium sulphate by solution of the sample in nitric-hydrochloric acid, followed by evaporation to dryness in the presence of potassium nitrate. After baking to remove nitric acid, the residue is dissolved in hydrochloric acid, and the solution treated with zinc to reduce iron. The ferrous iron solution is filtered and sulphur precipitated as barium sulphate from dilute hydrochloric acid solution. The weight of the ignited barium sulphate is corrected for blank and converted to sulphur content.

(c) Estimation of silicon.

Silicon was estimated by a standard procedure[88]. The alloy was dissolved in conc. hydrochloric acid and then evaporated to dryness and baked. The residue is redissolved in conc. hydrochloric acid and the solution is diluted and boiled, and the silica was filtered off on an ashless paper pad. The residue was transferred to a platinum crucible, dried and ignited at 1100°C, then cooled and weighed. A mixture of 1 ml. sulphuric acid and 2 ml. hydrofluoric acid is added to the residue, which is then fumed to dryness and ignited, cooled and reweighed. The difference between the two weighings being the amount of silica, from which the silicon content was calculated.

PREPARATION AND ANALYSIS OF REACTION GASES.

The gases used in this investigation were either mixtures of argon and sulphur dioxide, or of argon, sulphur dioxide and carbon dioxide.

It was decided to carry on the experiments using a gas flow rate over 4 litres per minute, so as to be quite sure that the rate of sulphur pick up by the molten metal would be independent of the gas flow rate. It was also decided to work with a gas mixture in which the SO_2 content does not exceed 1%. It was found that with gas mixtures with SO_2 content over 1% most of the sulphur was picked up by the metal and it was very difficult to get a clear picture of the rate of sulphur pick up.

With these restrictions in mind, and since the investigation depended on the estimation of the sulphur potential in a certain volume of gas mixture both before and after the runs, it was necessary to evolve a method of preparing a gas mixture with a definite stable composition throughout each experiment.

Using the conventional methods of gas metering and mixing proved quite unsatisfactory. At first 5 foot capillary meters (using G.T. manometer oil) were used in metering argon and SO_2. The high purity argon from the cylinder was dried in a drying tower containing lump $CaCl_2$.(Sulphuric/acid scrubbers could not be used in this case since at the high argon flow rate the gas would carry away with it H_2SO_4 fumes).

From the flowmeters, argon entered the mixing chamber which consisted of cylindrical glass tube containing magnesium perchlorate and glass beads. Sulphur dioxide was used from a siphon, and before it was metered, the gas was dried in a H_2SO_4 bubbler, then passed through a tower containing silica gel and magnesium perchlorate to complete the drying of the gas and to remove the H_2SO_4 mist carried over from the H_2SO_4 bubbler. After metering SO_2 entered the mixing chamber, where after admixture with argon, it was led either to the reaction chamber or to the analysis system or to waste as required. However, due to the very big discrepancy between the argon pressure and SO_2 pressure (argon 5 litres per minute, SO_2 6 Ml. per minute), it was extremely difficult to control the gas composition. Serious leaks developed whenever a change in the direction of gas flow was made. In some cases, the SO_2 flowmeter did not register at all due to the high back pressure of argon. Measures to remedy this were tried. In one case, a capillary tube was used to lead SO_2 to the mixing chamber, while a big diameter glass tube was used for argon. This was done to try and equalize the back pressure of the two gases. In another trial, the SO_2 flowrate was controlled by a needle valve by the manipulation of which a high back pressure SO_2 was obtained. However, none of these methods was successful. The control of gas composition was very difficult and a homogeneous composition throughout the run was never obtained, and generally it was not practical to do any investigation using this set up.

The solution adopted was to mix the gases in a storage chamber, the capacity of which was large enough to contain sufficient gas for a complete experiment. The gas mixture could then be drawn off as required. SO_2 was dried and then metered through a flowrator (Fischer and Porter indicating variable area flow meter). SO_2 was then pushed into a rubber container whose capacity was 150 litres . High purity argon, was metered, in a wet gas meter which accurately measures the volumetric discharge of gases, and was then pushed at high flow rate into the rubber container. The turbulence caused by the high flow rate of argon was enough to ensure a thorough mixing of the gases. The gas mixture was then drawn off with the help of a pump at the flow rate required. In the experiments where CO_2 was used, it was also metered into the rubber container before the admission of argon.

Although SO_2 attacks rubber, it was found that the rate of sulphur loss becomes constant with time, so that with experience, it was quite easy to calculate the amount of excess SO_2 to be added, to give a certain sulphur potential at the time of the experiment. (The advantage of the rubber container was that the gas mixture was always at the same pressure throughout the experiment. This pressure was slightly less than atmospheric pressure).

Analysis of the reaction gases.

The determination of the sulphur potential in the inlet and outlet gases, was effected by passing the gases through jars containing a 4 volume solution of hydrogen peroxide, where the sulphuric acid formed was titrated against standard solutions of KOH using methyl orange as indicator. Methyl orange was suitable as indicator in this titration because it was not affected by CO_2.

Hydrogen peroxide was very efficient in absorption of SO_2, so that most of this gas was absorped in the first jar.

In the beginning of this work, another method for the determination of SO_2 was used. The gas was passed through jars containing acidified water and 2 ml of starch solution. Into the gas absorption jars, projected the nozzles of burettes containing a standard solution of KI/KIO_3. This arrangement was used so that the absorpred SO_2 would be titrated continuously throughout the passage of the gases, ensuring an efficient determination of SO_2. However, due to the high flow rate of the gas stream, and to the resulting high gas pressure inside the absorption jars, the KI/KIO_3 solution could not pass down into the jars and gas bubbles pushed the KI/KIO_3 solution up in the burettes.

To remedy this a known volume of standard KI/KIO_3 solution was added to every jar, before the run, and was back titrated against standard sodium thiosulphate solution to determine the amount of

KI/KIO_3 affected by S_xO_y. This method, however, gave much higher results over what might be expected from the amount of SO_3 initially added to the gas mixture. When pure argon was passed through the absorption solution containing KI/KIO_3, for a time and at a flow rate comparable to the experimental one, a loss of KI/KIO_3 solution was registered. This was very surprising, and since pure argon could not be oxidising, the only explanation would be that a part of the iodine liberated in the acid solution was swept away by the gas due to the high flow rate used. Thus it was decided to use the hydrogen peroxide method.

Determination of CO_2 in the exit gases.

An attempt was made to determine the rate of carbon loss from the samples by oxidising CO in the exit gases to CO_2, and determining carbon as CO_2. The oxidising agents used were CuO at 600°C and activated MnO_2. All the attempts however were unsuccessful. The high flow rate did not allow enough contact time between CO and the oxidising agents. Attempts to collect gas samples and then analyse the gas for CO_2 did not solve the problem since this method gave different results on duplication.

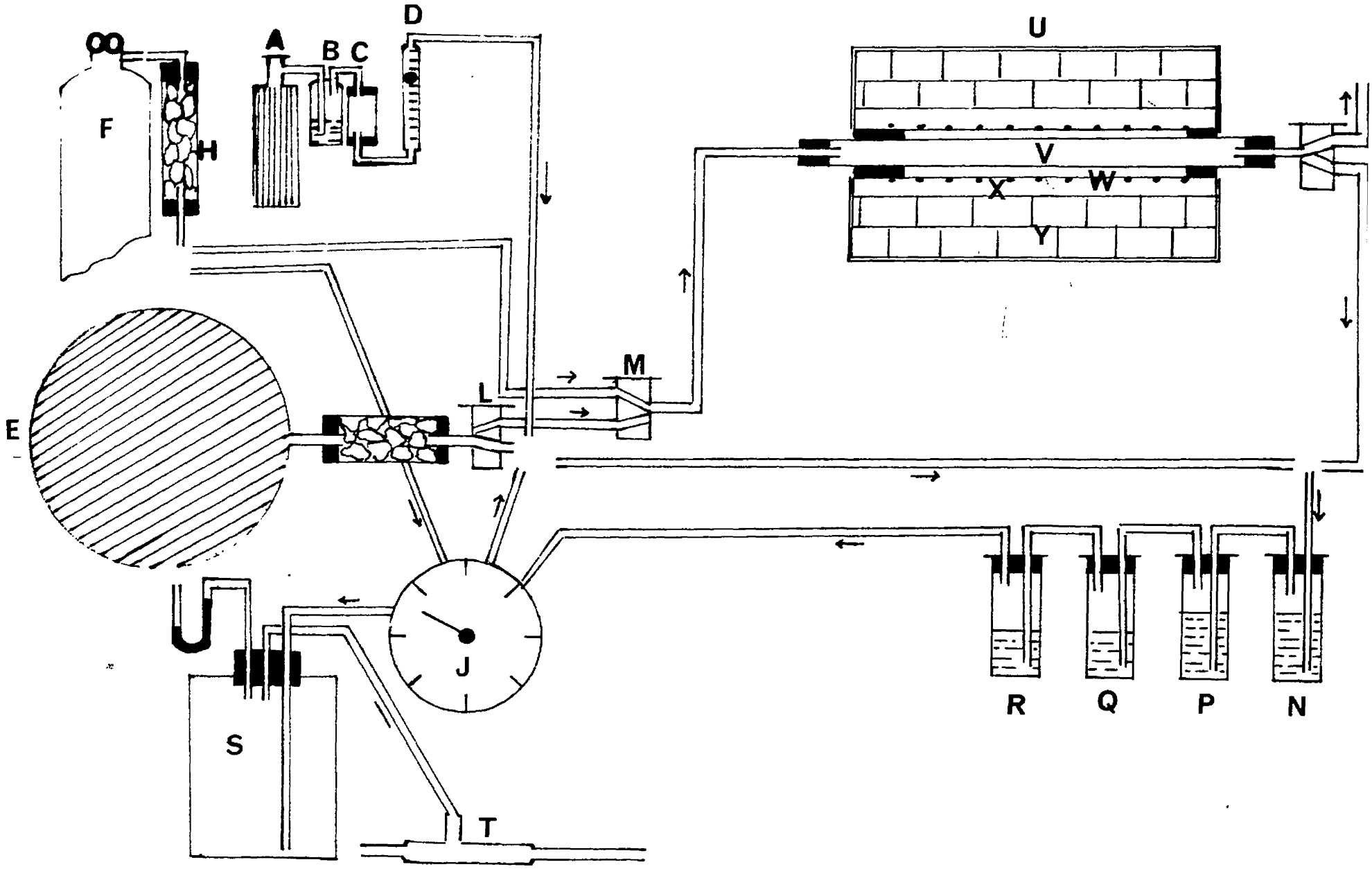

Figure 1

Crucibles

Three types of crucibles were used.

1. Recrystallized alumina boats chosen in such a way as to give variable surface areas and depth of samples.
2. Rough alumina boats formed by shaping from a paste of alundum powder and firing at high temperature.
3. Graphite boats formed by machining from a graphite rod.

Apparatus

The apparatus used in this investigation was simple, and allowed easy control of the experimental conditions. Fig. (1.) is a sketch of its main features.

SO_2 gas is led from siphon A to a bubbler B containing H_2SO_4, and then through a drying tower C containing silica gel and magnesium perchlorate. SO_2 is metered by a flowrator D from which SO_2 could be led via a detachable P.V.C. tube to a two-way tap L connected to the rubber storage container E. Argon gas from cylinder F is dried in drying tower H containing lump $CaCl_2$. Argon could either be connected to the reaction chamber V via a two way tap M, or argon could be connected to a drum shaped wet gas meter J, from which the metered gas is led via two-way tap L to the rubber storage tank E. This rubber container had 1/8" walls and was easily deflated, so that as the gas is sucked from it, the walls deflate, and the gas inside the container is always at the same pressure.

The gas mixture could be sucked through two way tap L to the gas analysis sytem consisting of jars F and H containing a 4 volume solution of hydrogen peroxide which strips the gas stream from its SO_3 content. The gas is then led through two scrubbers R and Q, containing chromo-sulphuric acid. This was a precautionary measure against the corrosion of the gas meter by any escaping SO_3. The gas is sucked through the wet gas meter J, and through a ballast tank with a simple mercury manometer S to a water suction pump I of the type used as filteration aid in chemical laboratories. A graduated disc and a pointer attached to the pump, served as a rough guide to the flow rate, which was measured accurately by the wet gas meter. The ballast tank served as a stabilizer of the gas flow and the manometer S gave a measure of the gas pressure which was invariably 2 ml. of mercury at 5 litres per minute flow rate.

The gas mixture could also be led through two way taps L and M to the reaction chamber V, and hence either to the analysis system or to waste. The reaction furnace U was a platinum wound resistance type, with the tube in a horizontal position. The furnace tube was a 30" long, 1.1/8" internal diameter, recrystallised alumina one. This was placed within a thin alundum tube on which was wound 20 s.w.g. platinum wire ½" The winding was insulated by fused alumina X and diatomaceous brick Y.

This furnace gave at 1400°C - 1450°C a hot zone constant to within 5°C over a length of 2 inches. The power input to the furnace was controlled by a 16 ampere Variac auto transformer by adjustment of which and in conjunction with a Kelvin Hughes temperature controller, temperature would be maintained constant at the desired temperature ± 5°C.

The temperature was measured by a platinum-13% rhodium platinum thermocouple, housed in a mullite sheath which fitted between the reaction tube and the alundum tube. The thermocouple was regularly standardised against a calibrated platinum - 13% rhodium platinum one, using a Cambridge potentiometer.

Experimental Procedure

An argon/sulphur dioxide gas mixture containing a certain sulphur potential, with or without the addition of CO_2 depending on the experimental conditions desired, was prepared some hours before the beginning of the experiment. By this time, the sulphur loss to the rubber storage container walls, would settle down to a very low value, and the change in sulphur potential in the reaction gas mixture coming from the rubber container would not be significant during the experiment.

The desired weight of the alloy sample was loaded in the boat used in the experiment. The loaded boat was then pushed carefully inside the furnace reaction tube to the hot zone position. The furnace was switched on, and a stream of 100 ml. per minute argon was used to flush the reaction chamber, and during heating up.

The furnace took 3 to35 hours to reach the desired experimental temperature. Before this temperature was reached, the gas storage container was connected to the gas analysis system and three analyses were made for the sulphur potential in the gas mixture. These three analyses invariably showed very good agreement.

Every three runs, in one experiment, and at the end of the experiment, the stock gas mixture was also analysed. These analyses showed that the gas mixture was homogenous throughout the experiment.

When the furnace reached the desired temperature the exit end of the reaction tube was sealed, the argon flow stopped, and the gas storage container was connected to the reaction chamber. The exit end of the reaction chamber was connected to the gas analysis system. Instalments of five litres of gas mixtures were sucked through the reaction chamber and over to the gas analysis system at

a certain flow rate. The exit end of the reaction chamber was then sealed off and the difference in sulphur potential between the inlet and outlet gases was determined by titration of the absorption solution against $\frac{N}{10}$ KOH. This was done every three minutes and the experiment was finished when the sulphur pick up became constant at a certain flow rate. The difference in sulphur potential in five litres of reaction gas, before and after the run, was taken as a measure of the amount of sulphur pick up by the sample.

After finishing the experiment, the reaction chamber was flushed with argon, and sealed off. After cooling, the solid sample was crushed and analysed for carbon and sulphur.

RESULTS

Results

In this work an attempt was made to evaluate some of the factors affecting the absorption of sulphur by liquid iron from atmospheres containing sulphur dioxide.

The experimental results obtained are represented as the average amount of sulphur pick up per unit gas volume (5 litres) per minute per gram of sample at a specified melt composition, gas composition, melt geometry, temperature and gas flow.

In the beginning of this work some exploratory experiments were done, whose purpose was to become familiar with the general characteristics of the sulphur pick up by liquid iron and to determine the best possible experimental conditions under which the aims of this work could be fulfilled.

The general course of sulphur pick up by the molten iron sample is typically illustrated by Fig. 2. Five litres of the gas mixture were passed over the sample every three minutes, and the difference in sulphur potential between the inlet and outlet gases, was taken as the amount absorbed by the metal. The first run registers a relatively big pick up by the sample. The next run after three minutes shows a much lower value. The subsequent runs show a gradual decrease in the amount of pick up till a stage is

reached at which the amount of pick up steadies up giving the same value for runs at 3 minute intervals. These 3 minute intervals were the minimum time between the runs in which the sulphur potential of the outlet gases from one run could be estimated and a fresh solution for the subsequent run is prepared. Fig. (2) shows that, the interval between the runs must be 30 minutes, before the value of sulphur pick up will be the same as that registered in the first run.

This behaviour was general in all the experiments, although the shape of the curve as in Fig (2) did differ in some experiments, the main difference being the number of runs carried out, i.e. the time taken till the steady pick up stage. At higher temperatures a slowness in reaching this stage was noticed. Also, the time taken to reach the steady pick up wasgreater when the sulphur potential in the reaction gas was low than when it was high. The carbon concentration in the melt also had an effect in this context. A lower carbon concentration was associated with more rapid approach to the steady pick up. However, the most noticeable difference was observed when the melt contained silicon. Here the higher the silicon content, the more rapid was the approach to the steady pick up stage. With samples containing 5·6 % silicon the pick up was found to be constant after only one run. In all

samples containing silicon, graphitisation occurred. From this behaviour it appears that the melt picks up sulphur in a greater amount at first, till a sulphur rich layer is formed, from which sulphur diffuses very slowly down to the bulk of the metal. When this sulphur rich layer is formed, the sulphur pick up becomes steady and its amount is dependent on the rate of diffusion of sulphur from the sulphur rich layer into the melt. This rate is dependent on temperature, the gas sulphur potential, and the melt composition (given in an order of increasing importance).

Henceforth all the results which are given will refer to the steady value obtained, i.e. for each experiment so many runs were done till the same value of sulphur pick up was obtained for 4 consecutive runs and this is the value taken as the value of sulphur pick up under the experimental conditions concerned.

It was decided to fix the boundary layer conditions at the gas/metal interface so as to limit the experimental variables, i.e. so that the pick up would be independent of gas flow rate. Various gas flow rates were tried keeping other experimental variables constant and as Fig. (3) shows in the range of 2 litre per minute to 6 litre per minute, the amount of pick up is independent of flow rate. The slight increase in pick up at higher flow rates reflects only the higher sulphur potential in contact with the melt per unit time at higher flow rates.

The first 24 experiments carried out were concerned with the establishing of the effects of the sulphur potential in the gas, the temperature and the ratio of melt surface area to sample weight on the amount of sulphur pick up by the liquid iron. In experiments 1, 2, 3 and 4, gas mixtures of argon and SO_2 containing 0·1%, 0·17%, 0·457% and 0·66% SO_2 respectively were passed at 1400°C over samples of liquid iron weighing 20 grams and having a surface area of 5 cm^2. This was repeated in the same order but at 1450°C in experiments 9, 10, 11 and 12. Fig. (4) shows the effect of the various partial pressures of SO_2 and of temperature on the amount of sulphur pick up per minute per gram of sample in the range of 4 - 6 litre/minute gas flow rate.

It could be seen that the amount of pick up is approximately proportional to the concentration of sulphur dioxide in the gas mixture and that the higher the temperature the greater the amount of pick up. This tendency is repeated in Fig. 5 and Fig. 6, Fig. 5 being the results of experiments 5, 6, 7 and 8 at 1400°C, and 13, 14, 15, 16 at 1450°C for a sample weighing 10 grams and having a surface area of 3 cm^2. Fig. (6) represents the results of experiments 18, 17, 19, 20 at 1400°C and 21, 22, 23, 24 at 1450°C for a sample weighing 5 grams and having a surface area of 2·2 cm^2.

Comparison of Figs. 4, 5 and 6 shows that the pick up for the 5 gram samples having a surface area to weight ratio of 0·44 was higher than in the corresponding 10 or 20 gram samples having surface area to weight ration of 0·3 and 0·25 respectively. However, the relation is not clear or consistent in comparing the 10 and 20 gram samples. Generally, the effect of temperature and surface area to weight ratio is clearer for the experiments in which higher sulphur potential, i.e. 0·457% and 0·66% SO_3 were used than in the experiments where gases with 0·1% and 0·17% SO_3 were used. In this case as the graphs show the lines are too close together and the difference in pick up is well within the range of experimental error.

A number of experiments was done to examine the effect of change of pO_2 in the gas atmosphere on the amount of sulphur pick up.

In experiment 33 a machined graphite shield with perforations in it was put in the hot zone of the furnace just before an alumina boat containing 10 grams of 4·27% carbon iron. It was hoped that this arrangement might help in examining the effect of reducing pO_2 in the gas atmosphere to a very low value. An argon-sulphur dioxide gas mixture containing 0·66% SO_3 was passed over the sample and according to the general procedure the amount of sulphur pick up at flow rates in the rage of 4 - 6 litres/minute of gas flow was estimated. A surprisingly high result was obtained, e.g. at 5 litres

per minute flow rate, the estimated pick up was found to be about 260×10^{-5} grams sulphur per gram of sample per minute. This was about as much as five times the amount of pick up by the same sample under the same experimental conditions but without the graphite shield.

In experiment 35, the same procedure as in experiment 33 was repeated, using an argon-sulphur dioxide gas mixture containing 0·17% SO_2. In this case also the amount of pick up was found to be about eight times bigger than that for a comparable sample without the graphite shield.

In experiment 31, a graphite boat was used as a container for the sample. The graphite boat was machined in such a way as to give a 3 cm^2 surface area for a 10 gram sample. A 0·66% SO_2 gas was passed over the sample at 1400°C. In experiment 32, a 0·17% SO_2 gas was used repeating the same procedure in experiment 31. The amount of pick up appeared in both cases to be higher than that in comparable experiments using alumina boats but smaller than that in the experiments where the graphite shields were used. The analysis of samples in experiments 33, 35, 31 and 32 showed a very high discrepancy between the actual sulphur content of the metal and the value that would have been there if the experimental values of sulphur pick up were true.(Appendix). It seems certain that the very high value of pick up in the above four experiments must be attributed to the pick up of sulphur by the very active surface of the graphite

shield or boat, and that the seemingly orderly difference in pick up between the graphite shield experiments and the carbon boat experiments were merely due to kinetic factors, namely a bigger surface area of active carbon in case of the graphite shield.

In experiment 34, graphite powder was added to a 10 gram sample of 4·27% carbon iron and charged in an alumina boat giving 3 cm^2 surface area to the molten sample and 0·66% SO_2-argon gas mixture was passed over the sample at 1400°C. The amount of sulphur pick up was found to be higher than a comparable sample with no graphite powder added, e.g. at 5 litre/minute the pick up for the sample with graphite powder is about 70 x 10^{-5} grams sulphur while that of a comparable sample without the graphite powder is about 60 x 10^{-5}. This tendency is consistent at the other flow rates examined in experiment 34 and in experiment 36 where the same procedure as in experiment 34 was used but using a gas mixture with 0·17% SO_2. In both experiments the graphite powder was still there at the end of the experiments, and the analysed sulphur content agreed with the estimated sulphur content calculated from the results of the experiments (34, 36). This analysed value of sulphur was also very near to the analysed value of sulphur in the comparable experiments in which carbon boats and graphite shields were used. It is believed that the results of experiments 34, 36 give the true picture for sulphur pick up in which the carbon activity is kept at unity

throughout the experiment, and since the final analysis of sulphur in experiments 31, 33 was very near to that in experiment 34 (the same relation holding for the 0·17% SO_3 experiments), so in the calculation of the rates of sulphur pick up in the experiments where carbon boats or shields were used, the data for the comparable samples with graphite powder were used instead of the apparently deceptive experimental data.

Fig. (7) represents the apparent sulphur pick up in experiments 31, 33 compared with the results of experiment 34 and the results of the comparable experiment 6. The general outlines of Fig. (7) are repeated in Fig. (8), representing the results of experiments 32, 35 and 36 compared with experiment 6.

The effect of increasing $p O_2$ in the reaction gas was also investigated. In experiments 38, 40 and 41, 0·1%, 0·66% and 1% CO_2 were added respectively to a gas mixture containing 0·66% SO_2, and in all three experiments the sample was a 10 gram one containing 4·27% C. These runs were carried out at 1400°C and the amount of pick up was calculated in the usual way. The results of these experiments are shown in Fig. (9) compared with the values of pick up for a comparable sample with no CO_2 in the gas mixture. As could be seen from Fig. (9) the amount of pick up is lowered by addition of CO_2 to the gas mixture, and the effect is relative to the $p SO_2$ added.

The relative effects of increasing pO_2 in the gas mixture by adding CO_2 and the effect of lowering the carbon content of the sample were examined. In experiment 42, an argon-CO_2 gas mixture containing 0·66% CO_2 was passed at 1460°C over a 10 gram sample having a surface area of 3 cm^2 and containing 2·97% carbon. The amount of pick up in the 4-6 litre/minute flow rate range was estimated and the results of this experiment is represented in Fig. (10) compared with the results of experiments 41 and 8. Fig. 10 shows that the lower carbon content in experiments 42 a bigger effect in decreasing the amount of pick up than the addition of 0·66% CO_2 to the gas mixture. The same pattern was found when the above experiments were repeated at 1450°C. in experiments 48, 50. This higher temperature also allowed the use of a sample containing 2% carbon (experiment 49). In Fig (11) the results of experiments 48, 49 and 50 are compared with those of experiment 15, and although the values in this case are much closer together and could be within the range of experimental error, they however repeat the same patternof Fig (10). It appeared that at higher temperature, the effect of addition of CO_2 to the gas mixture, or lowering the carbon content, is smaller than these effects at lower temperature.

A set of experiments was carried out to evaluate the effect of increasing the depth of liquid melt. In experiments 53-59 the samples used were 20 grams, charged in alumina boats in which the

melt's depth would be 0·9 cm and the surface area 4 cm^2.

Experiments 53, 54, 58 were carried out at 1400°C. In experiment 53, the carbon content of the sample was 4·27% and the gas mixture contained 0·66% SO_2. In experiment 54 a sample containing 2·97% carbon was used and the gas mixture contained 0·66% SO_2. In experiment 58 the sample contained 4·27% C and the gas mixture contained 0·66% SO_2 and 0·66% CO_2. The above was repeated at 1450°C in experiments 55,,56 and 57. The amount of pick up was estimated in the usual way and the results of experiments 53, 54, 58 are shown in Fig. (12), and those of experiments 55, 56 and 57 are shown in Fig. (13). Here, although the lines are so close to each other as to be in the range of experimental error, however the same familiar pattern with respect to effect of temperature and the relative effects of additions of CO_2 and lowering the carbon content of the samples, is repeated again in these experiments.

In experiments 25 - 30 carried out at 1400°C, the sulphur pick up by iron, carbon silicon alloys was examined.

In experiments 27, 25, 29, where alloys containing about 4% carbon and 0·73% Si, 1·83% Si and 5·6% Si respectively were used, a gas containing 0·66 % SO_2 was passed over the samples and the amount of pick up was estimated. These experiments were repeated using a 0·17% SO_2 gas mixture in experiments 28, 26 and 30.

In all these experiments where silicon was present, powdered graphite was found in the corner of the boats nearer to the exit end, and from this it appears that the effect of silicon as a graphitizer was pronounced and that the carbon was precipitated as graphite while the samples were being melted as well as during solidification, otherwise the graphite powder would have been found on the surface of the solid metal and not in the corner of the boat (the samples were not cooled in a stream of argon, but the furnace was flushed with argon at high pressure and then sealed).. The results of experiments 27, 25, 29 are shown in Figure (14), those of experiment 28, 26 and 30 are shown in Fig. (15). From these data it looks as if the overall effect of additions of silicon is to increase the amount of pick up.

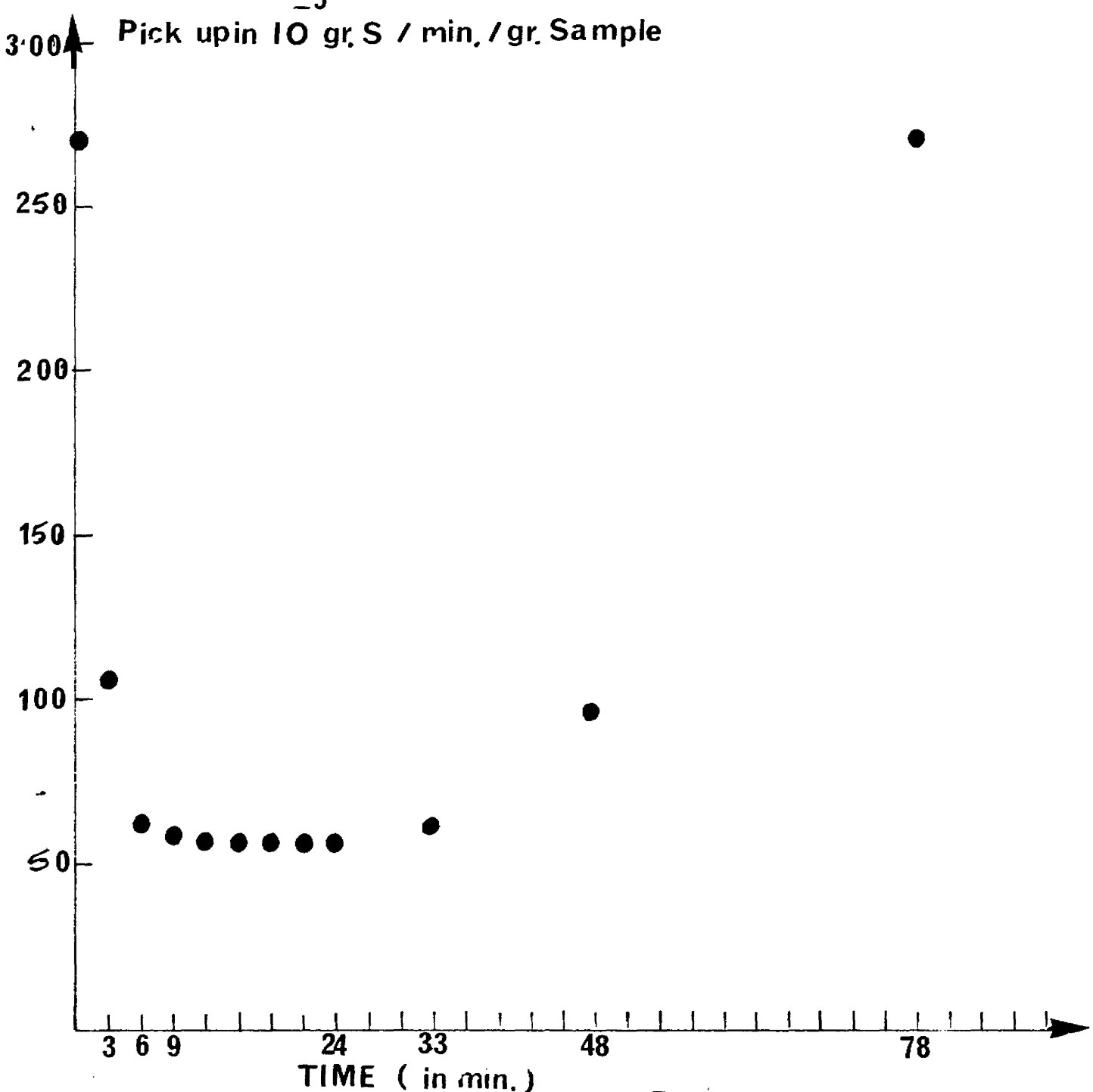
Pick upin IO gr. S / min. / gr. Sample
-5
300
250
200
150
100
50
3 6 9
24
33
48
78
TIME (in min.)

Figure 2

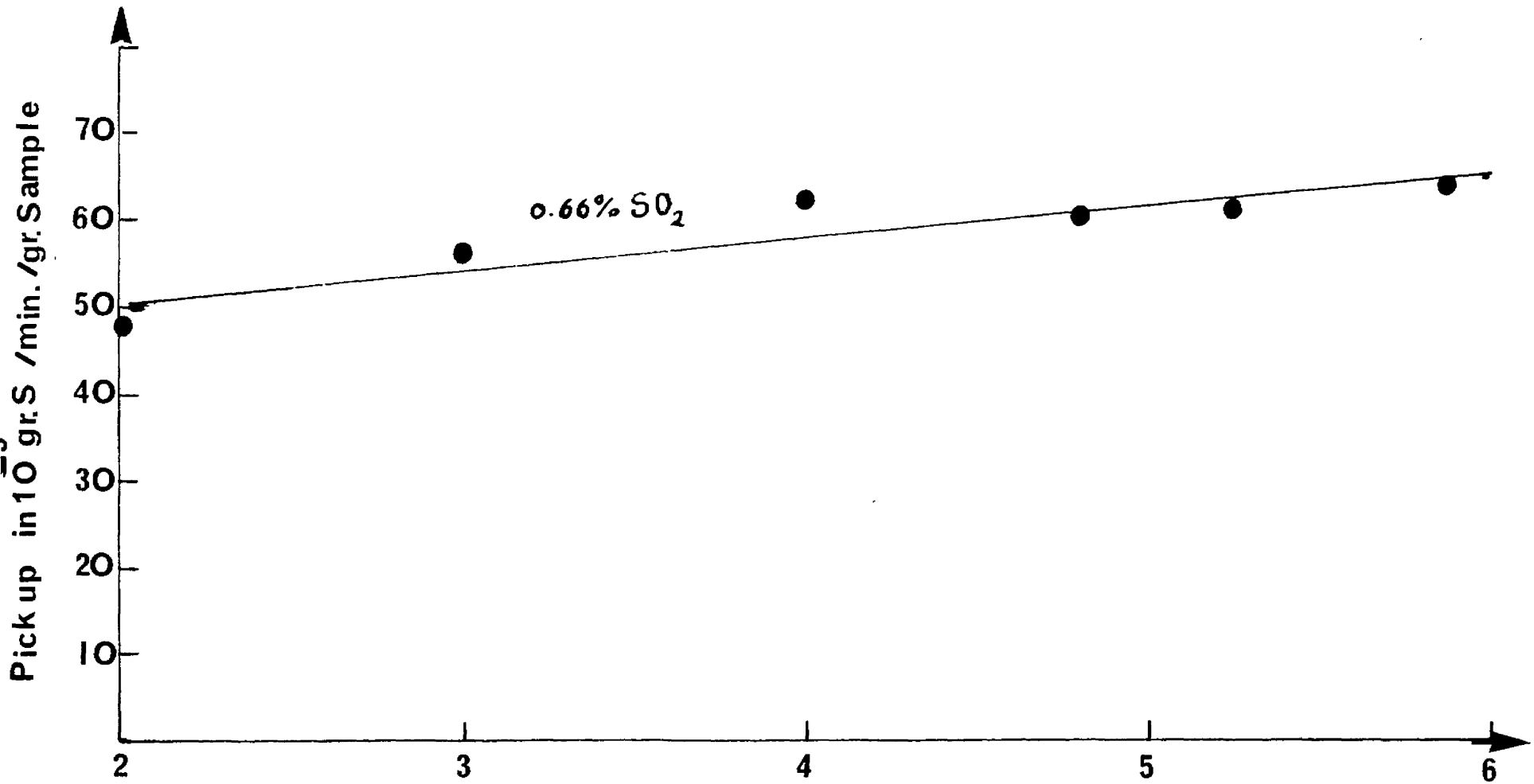
Pick up in 10^{-5} gr.S /min./gr.Sample
70
60
50
40
30
20
10
0.66% SO_2
2
3
4
5
6
FLOW RATE (litre/min.)

Figure 3

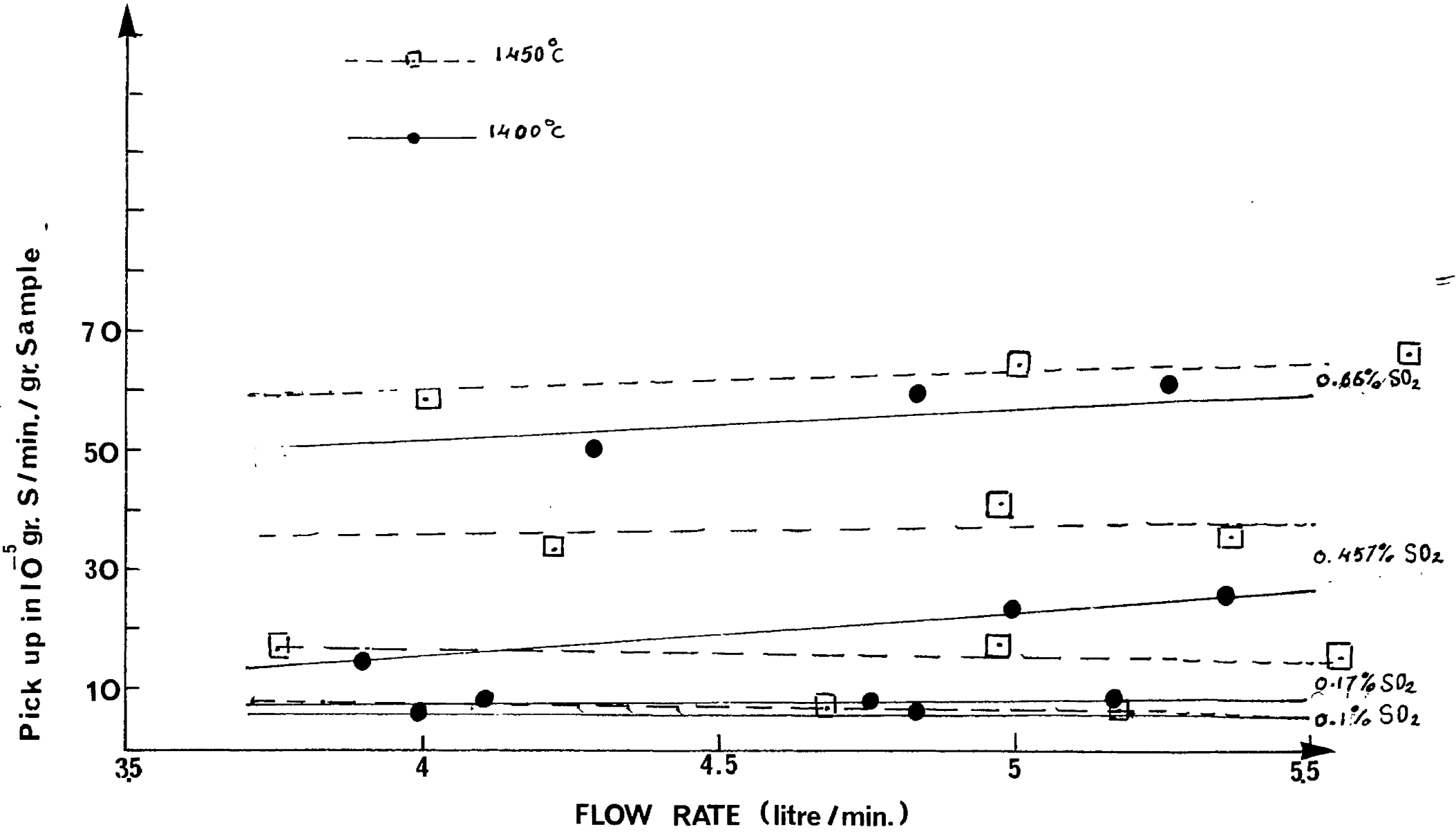
1450°C
1400°C
70
50
30
10
0.66% SO2
0.457% SO2
0.17% SO2
0.1% SO2
3.5
4
4.5
5
5.5
Pick up in 10⁻⁵ gr. S/min./gr. Sample
FLOW RATE (litre/min.)

Figure 4

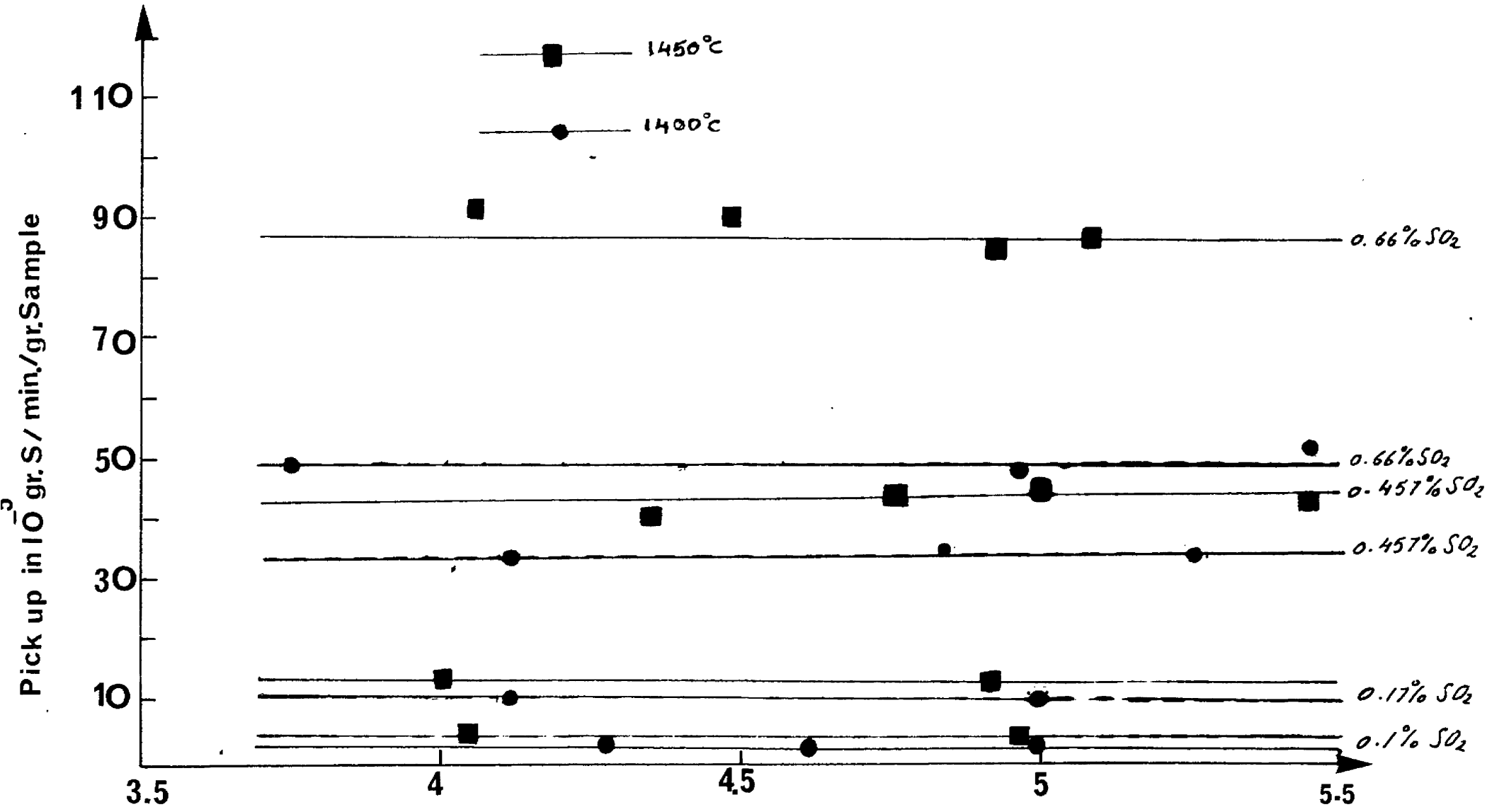
1450°C
1400°C
110
90
70
50
30
10
Pick up in 10⁻³ gr.S/min./gr.Sample
0.66% SO2
0.66% SO2
0.457% SO2
0.457% SO2
0.17% SO2
0.1% SO2
3.5
4
4.5
5
5.5
FLOW RATE (litre / min.)

Figure 5

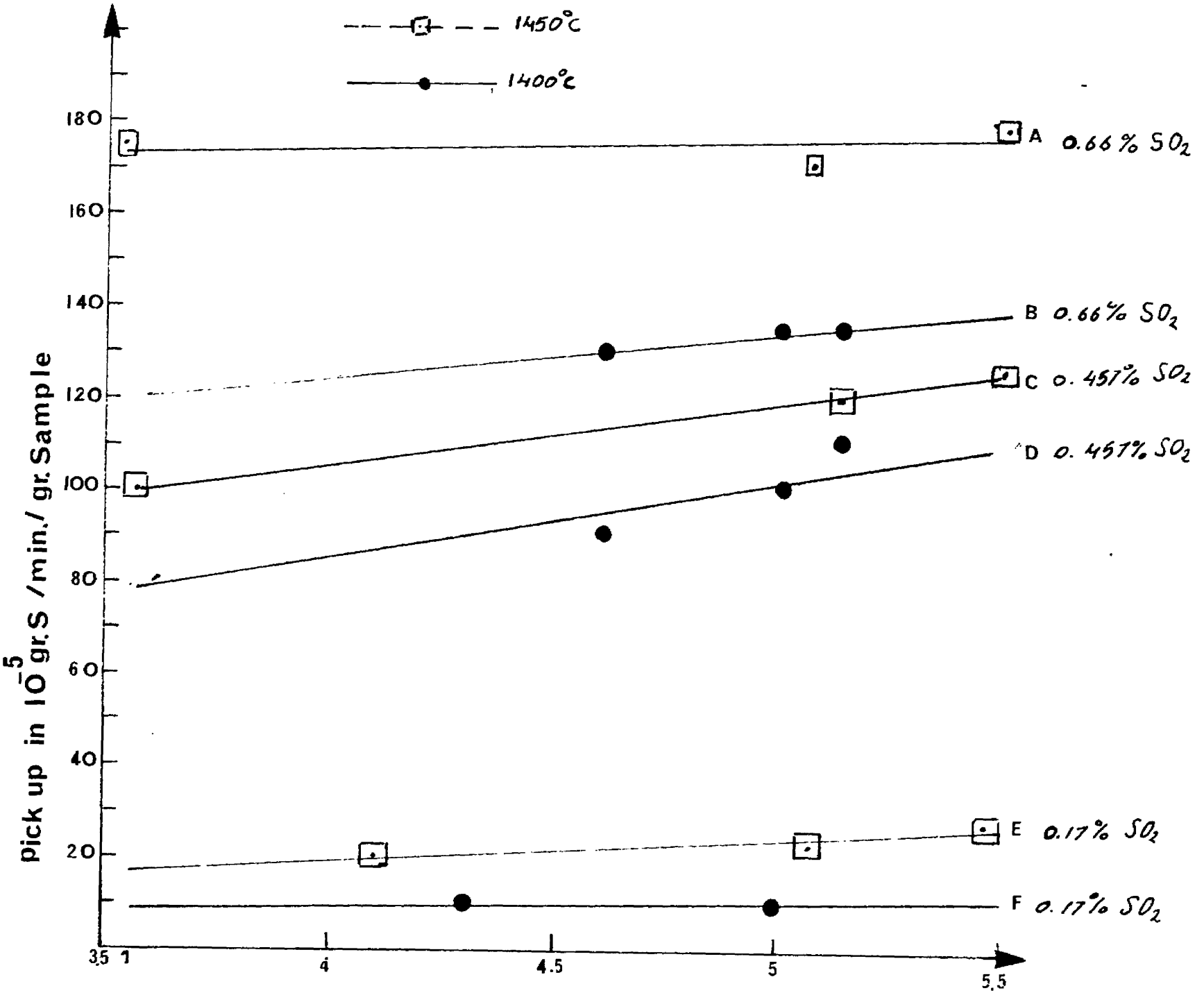
1450°C
1400°C
A 0.66% SO_2
B 0.66% SO_2
C 0.457% SO_2
D 0.457% SO_2
E 0.17% SO_2
F 0.17% SO_2
Pick up in 10^{-5} gr.S /min./ gr. Sample
180
160
140
120
100
80
60
40
20
3,5
1
4
4.5
5
5,5
FLOW RATE (litre / min.)

Figure 6

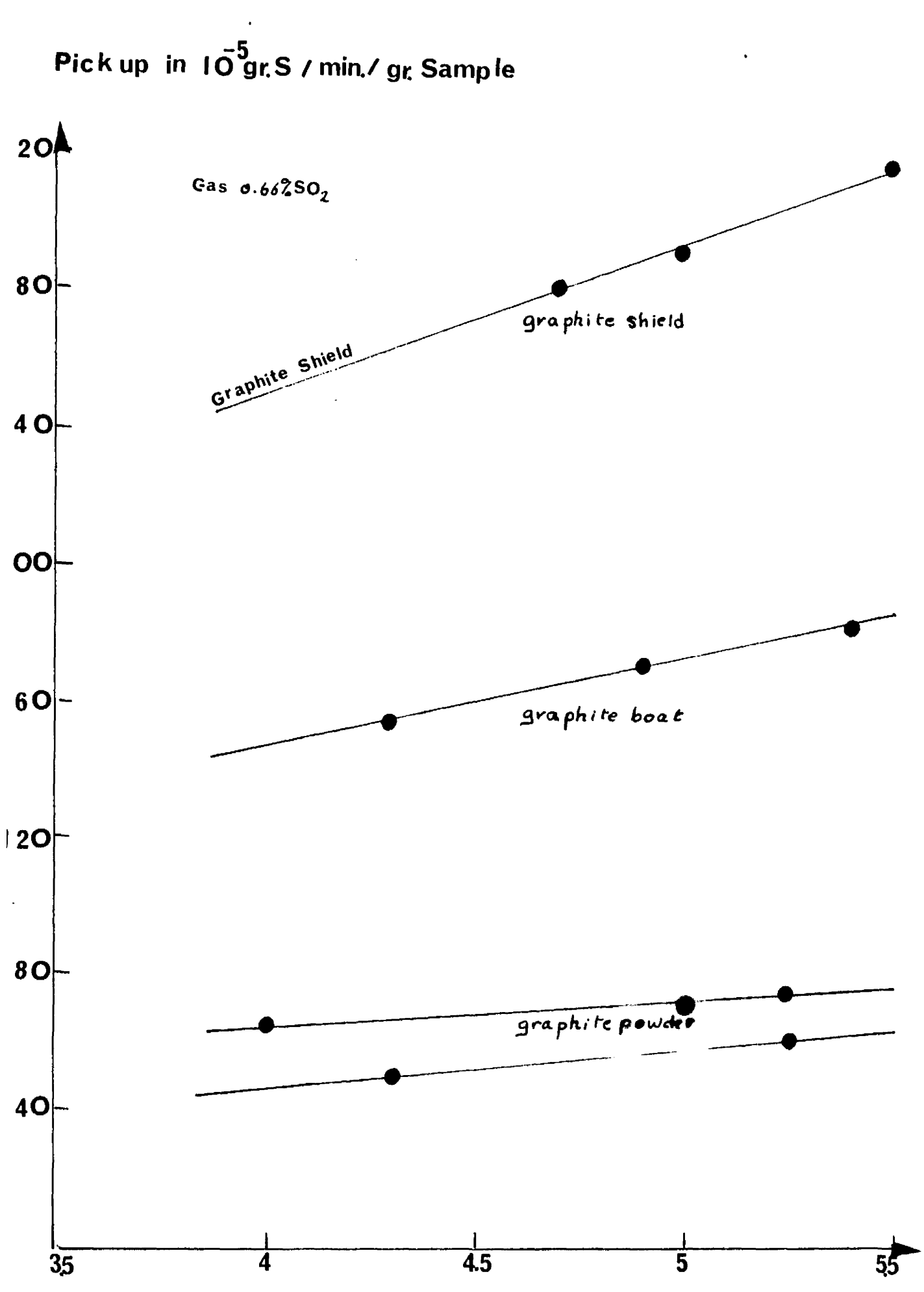
Pick up in 10^{-5} gr. S / min. / gr. Sample
20
80
40
00
60
120
80
40
Gas 0.66% SO_2
Graphite Shield
graphite shield
graphite boat
graphite powder
3.5
4
4.5
5
5.5
FLOW RATE (litre / min.)

Figure 7

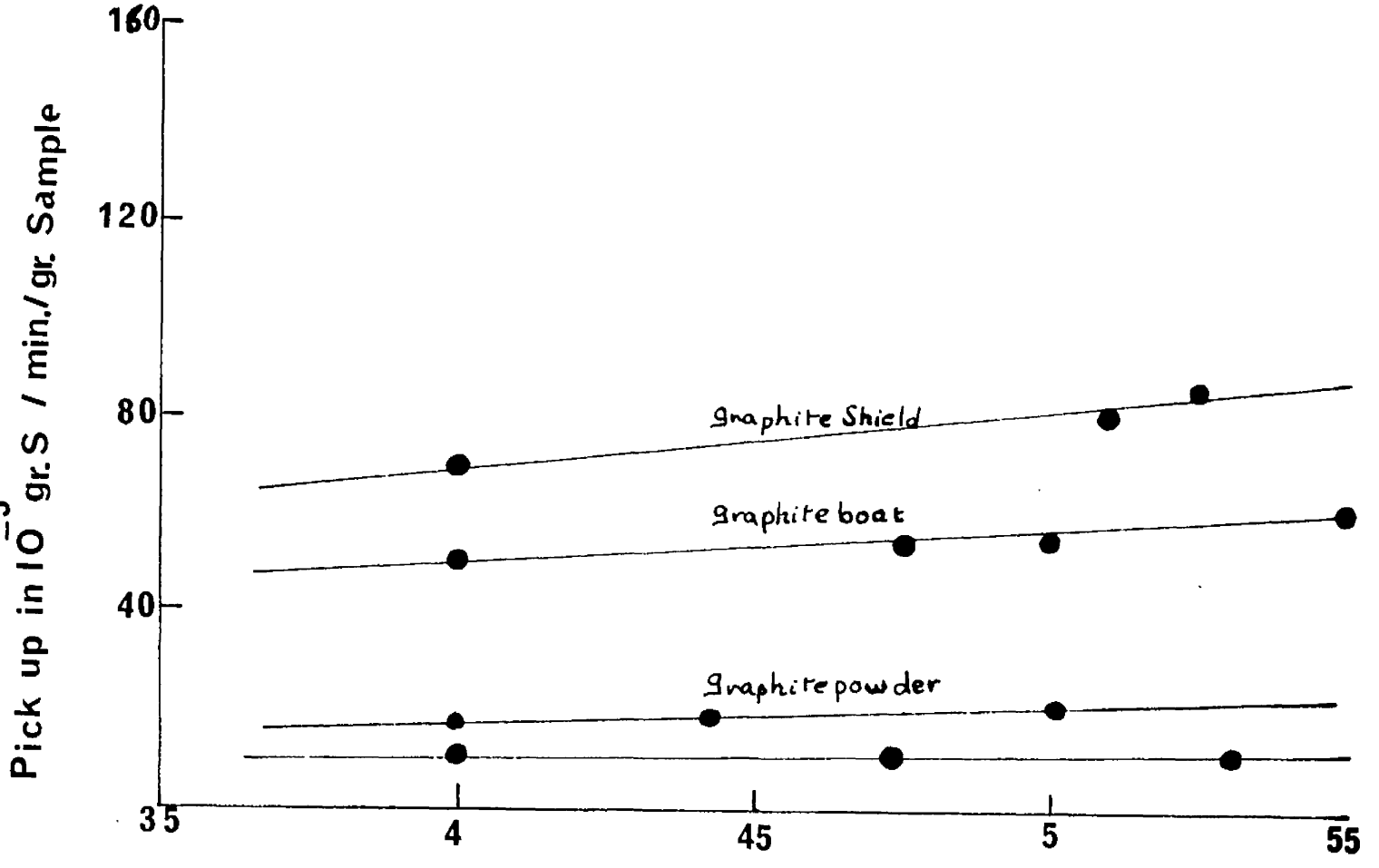
160
120
80
40
35
4
45
5
55
Pick up in 10^{-5} gr.S / min./gr. Sample
Graphite Shield
Graphite boat
Graphite powder
FLOW RATE (litre / min.)

Figure 8

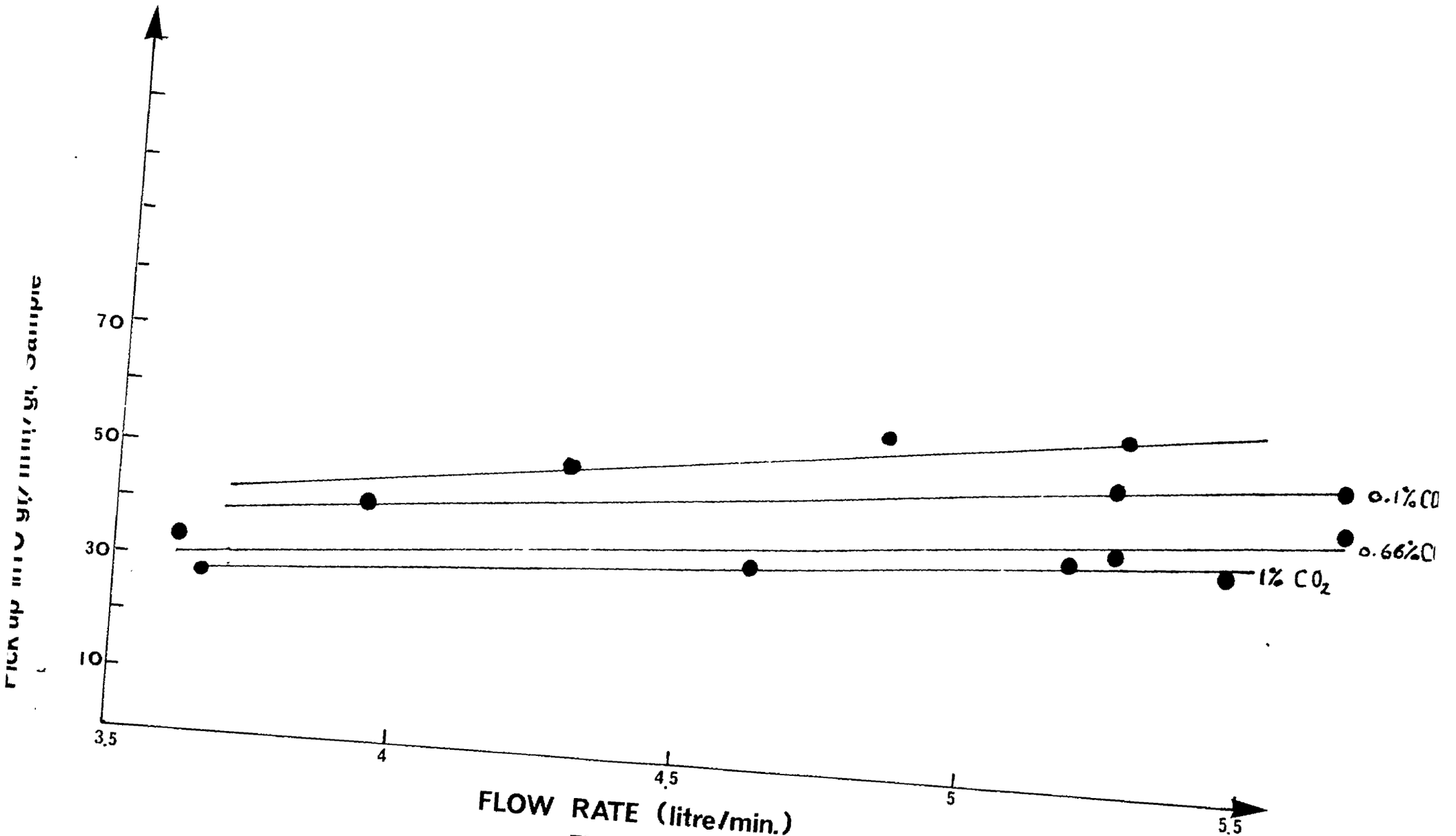

Figure 9

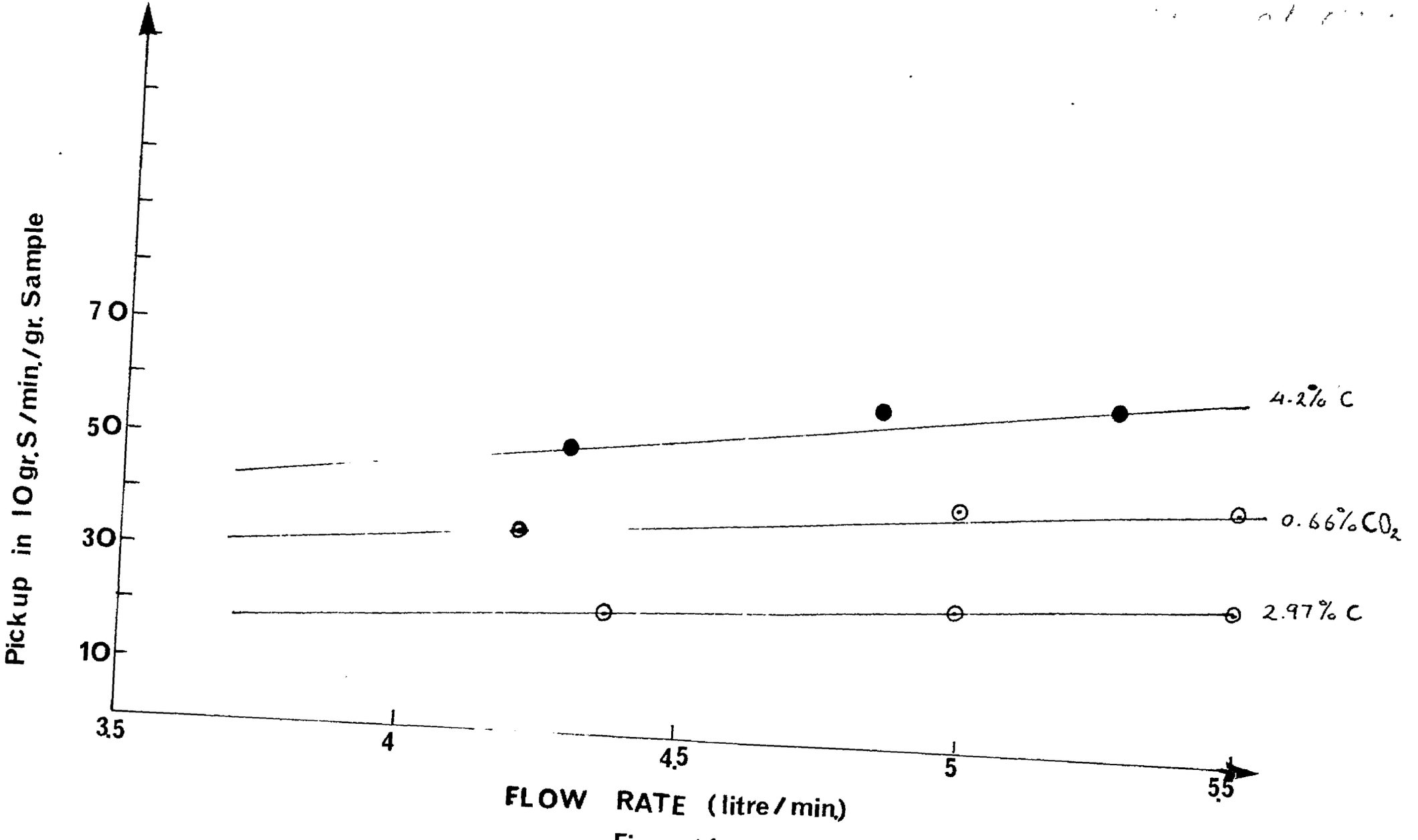
Pick up in 10 gr. S/min./gr. Sample
70
50
30
10
3.5
4
4.5
5
5.5
FLOW RATE (litre/min.)
4.2% C
0.66% CO_2
2.97% C

Figure 10

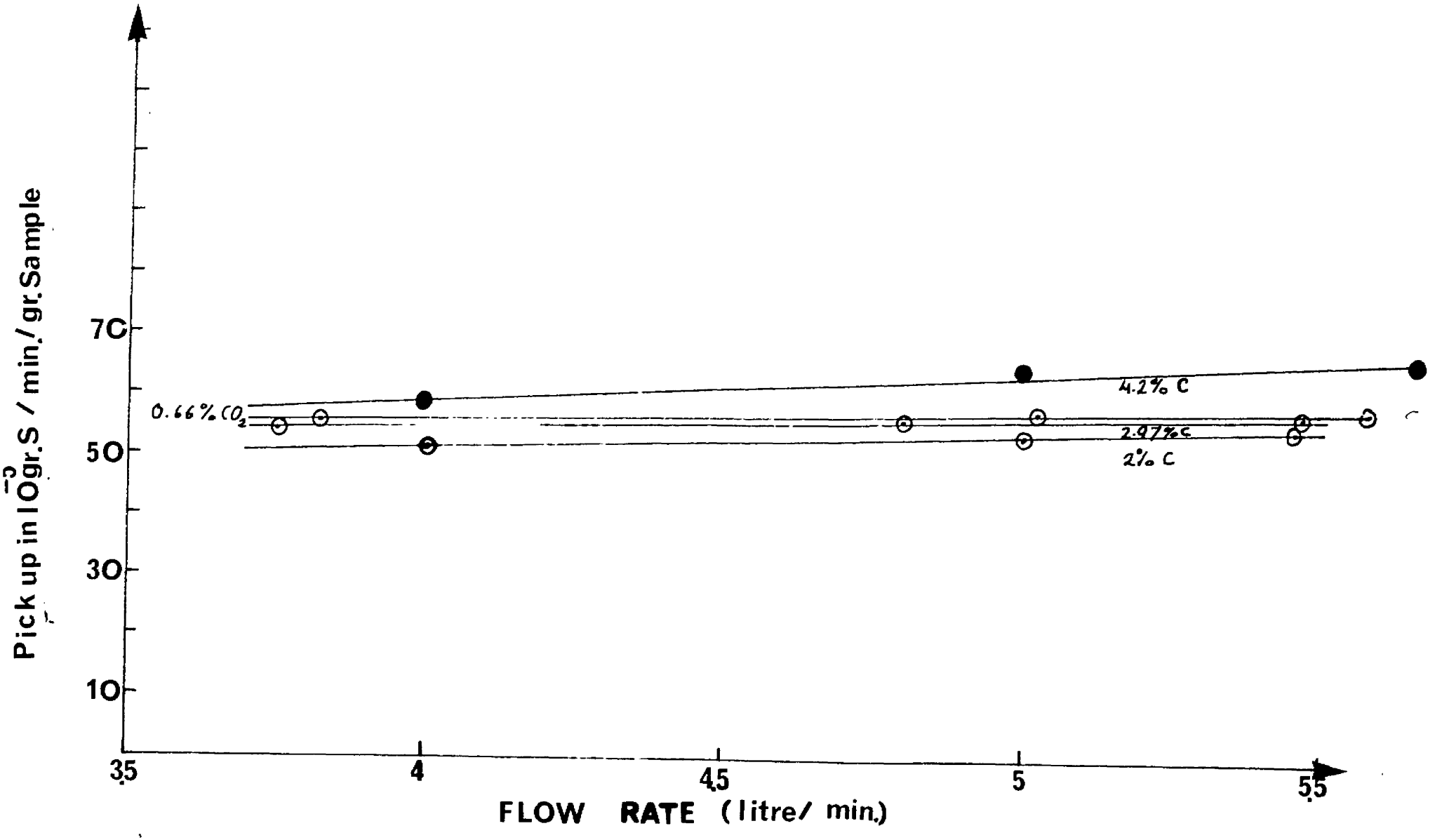
Pick up in 10^{-3} gr.S / min./ gr.Sample
70
50
30
10
0.66% CO_2
4.2% C
2.97% C
2% C
3.5
4
4.5
5
5.5
FLOW RATE (litre/ min.)

Figure 11

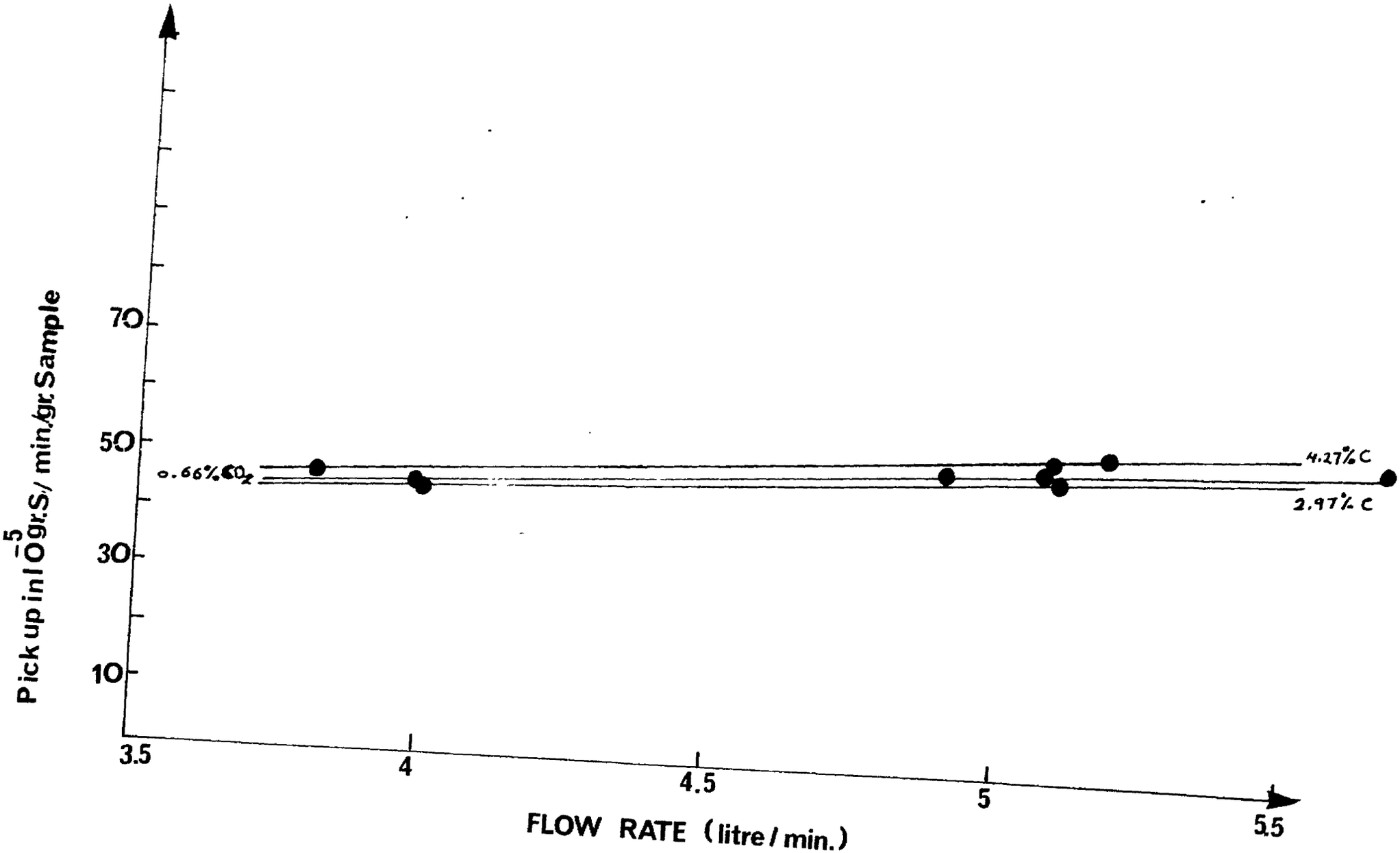
Pick up in 10^{-5} gr.S/ min./gr. Sample
70
50
30
10
0.66% CO_2
4.27% C
2.97% C
3.5
4
4.5
5
5.5
FLOW RATE (litre / min.)

Figure 12

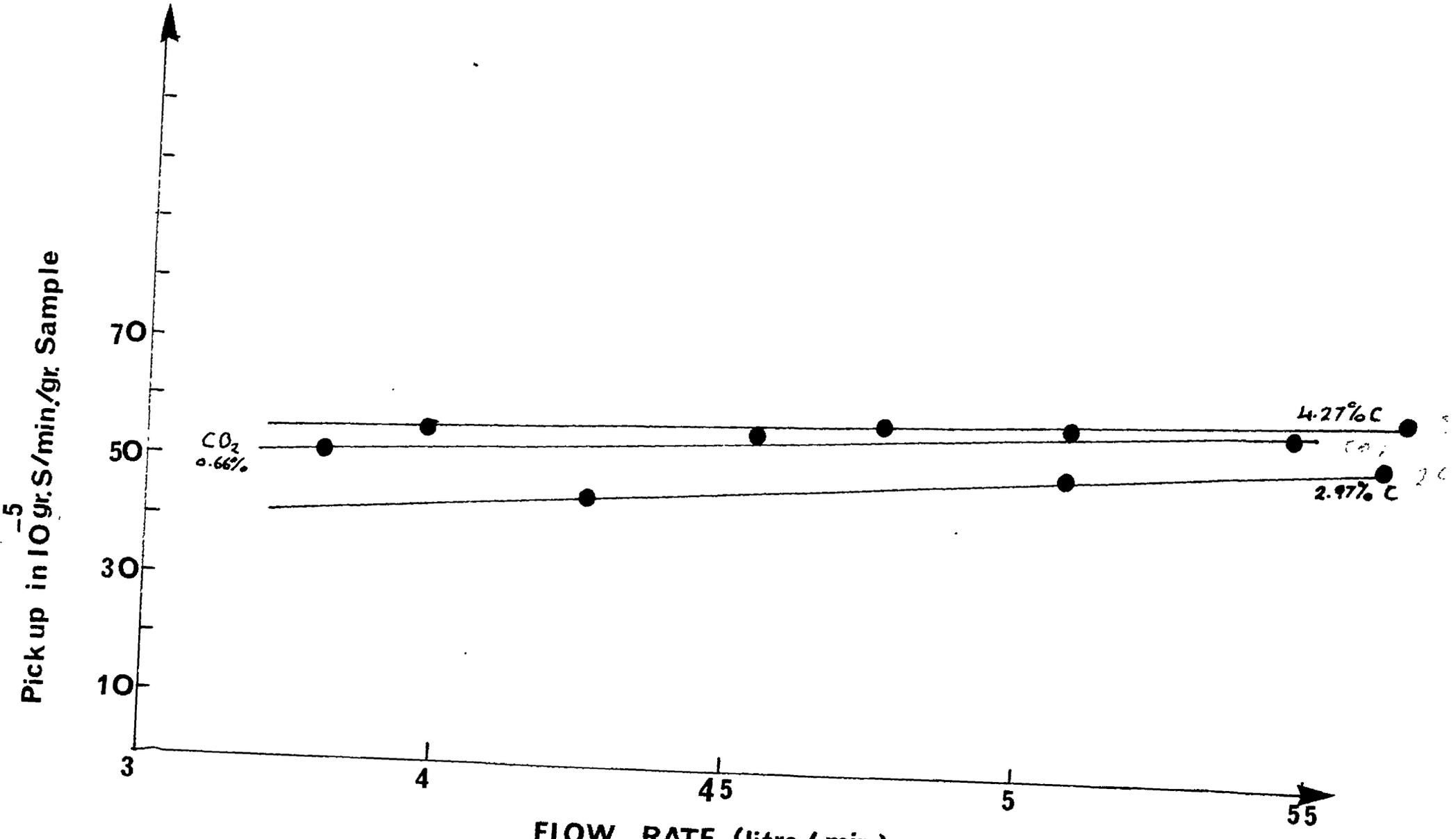
Pick up in 10^{-5} gr. S/min./gr. Sample
70
50
30
10
CO_2 0.66%
4.27% C
2.97% C
3
4
45
5
55
FLOW RATE (litre / min.)

Figure 13

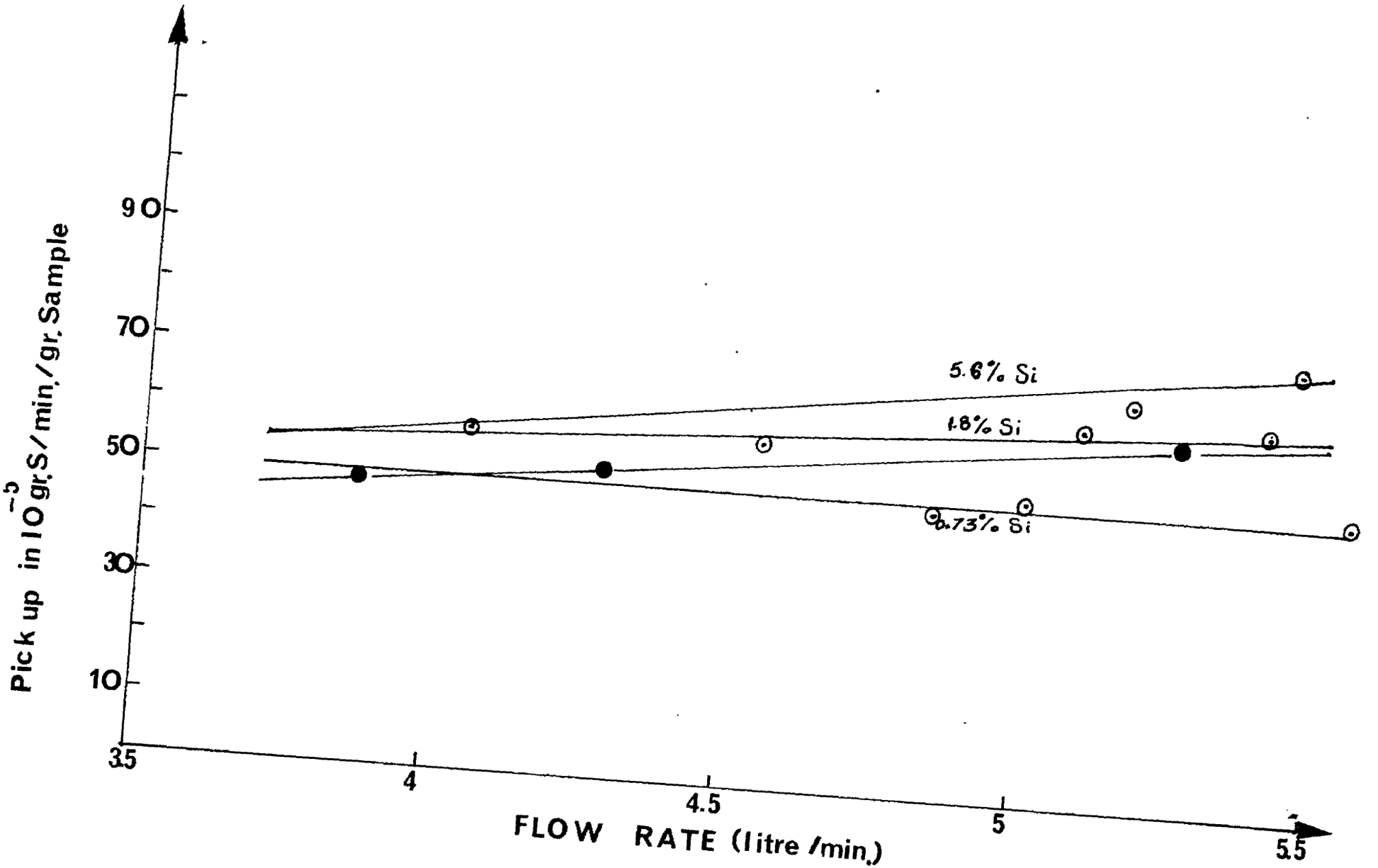
Pick up in 10^{-5} gr.S/min./gr.Sample
90
70
50
30
10
5.6% Si
1.8% Si
0.73% Si
3.5
4
4.5
5
5.5
FLOW RATE (litre /min.)

Figure 14

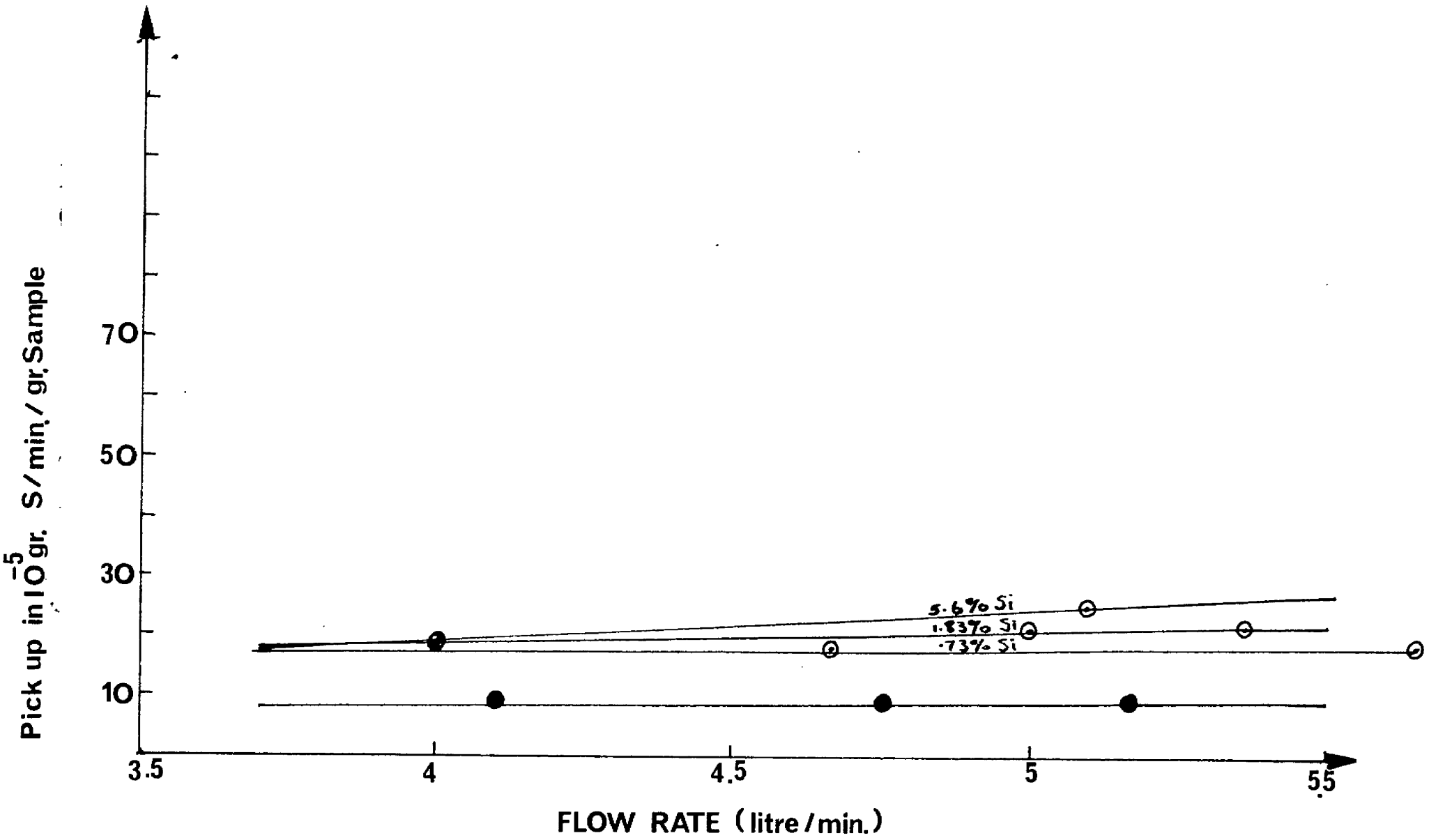
Pick up in 10^{-5} gr. S/min./gr. Sample
70
50
30
10
5.6% Si
1.83% Si
·73% Si
3.5
4
4.5
5
5.5
FLOW RATE (litre/min.)

Figure 15

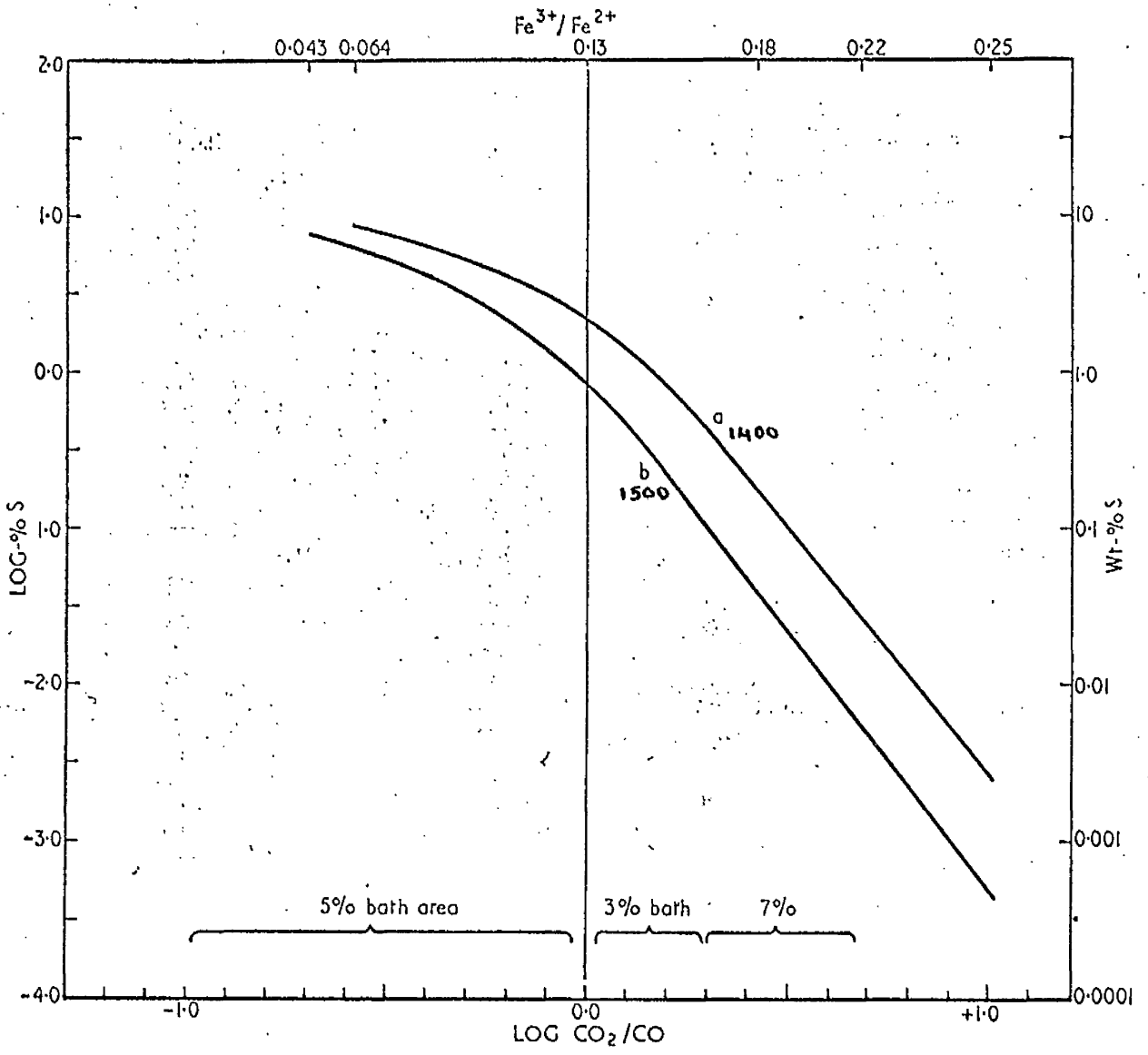
Fe^{3+}/Fe^{2+}
0·043 0·064
0·13
0·18
0·22
0·25
2·0
1·0
0·0
-1·0
-2·0
-3·0
-4·0
LOG-% S
10
1·0
0·1
0·01
0·001
0·0001
Wt-% S
a 1400
b 1500
5% bath area
3% bath
7%
-1·0
0·0
+1·0
LOG CO_2/CO

Fig. 16

CALCULATION OF RESULTS

Calculation of e_C

In the discussion of the results of this work the assumption has been made that there is local equilibrium between the melt and the gas film immediately adjacent to it, and that the overall reaction of the sulphur pick up by the metal is

$$SO_2 + 2\underline{C} = 2CO + \underline{S}$$

Thus the activity of carbon in the molten iron sample was necessary for the calculation of the partial pressures of the reacting gas species. This value was also needed in the determination of the f_S^C value and for the calculation of the oxygen flux. The initial carbon concentration was varied from one run to another according to the experimental conditions desired. Some blank runs were done, in which a sample with a known carbon content was heated up to the experimental temperature in a stream of high purity argon and then furnace cooled. Care was taken to simulate exactly the actual experimental conditions from the view point of heating up time, the volume and flow rate of argon, the weight of samples, the surface area of the melt, and so on. The analysis of these samples showed up a carbon loss varying from 0·4 to 0·5%. Since high purity argon was used in heating up and cooling down, it is very difficult to visualise the loss of carbon to be due to the presence of oxygen in the gas stream. The only

other explanations for the carbon loss would be the reaction of carbon with the crucible or the diffusion of oxygen, from or through the refractory tube at high temperature. If this explanation is to be accepted, and since the analysed sulphur content of the sample after the run, has been invariably less than that to be expected from the calculated experimental values, this could only mean that there must be also some loss of carbon during cooling. This argument is to illustrate the conclusion that neither the initial nor the final carbon content of the sample should be used in the calculation of e_g.

As has been mentioned elsewhere, the actual carbon loss during the runs could not be estimated due to experimental difficulties.

Thus it could be seen that the evaluation of the actual carbon concentration during the runs is very difficult and it was decided that a mean va lue between the initial and final carbon content is the most realistic choice.

The calculation of the Raoultian activity of carbon in liquid iron was according to the following procedure.

1. From the wt % C value, N_C and N_{Fe} were determined.
2. The Henrian activity coefficient of carbon in liquid iron was calculated according to Rist and Chipman[29] data

$$\log \gamma_C = \frac{4350}{T\,K}\left[1 + 4 \times 10^{-4}(T\,K - 1770)\right]\left[1 - N_{Fe}\right]$$

3. The Henrian activity was determined ${}^{a}C_h = \gamma_C \times N_C$

4. The carbon content at saturation for the experimental temperature was calculated from the formula given by Chipman et al[30]

$$[\text{wt } \% C]_{sat} = 1.34 + 2.54 \times 10^{-3} T^{\circ}$$

where T° is in centigrades.

5. The Henrian activity at saturation is calculated as above.

6. The carbon activity Raoult scale = $\frac{a_h}{a_h^{\circ}}$

where a_h is the Henrian activity and a_h° is the Henrian activity at carbon saturation.

Calculation of the partial pressures of reacting gas species.-

In some runs, the gas was formed of high purity argon, with which is mixed a certain percentage of SO_2. In other runs argon was mixed with fixed percentage of SO_2 and of CO_2.

When SO_2 is in contact with carbon saturated molten iron at high temperature, the following reactions may occur[31]

	Reaction	$K_{1873}{}^{\circ}K_{-15}$	$K_{1723}{}^{\circ}K_{-15}$
1.	$2SO_2 = S_2 + 2O_2$	1.0975×10	4.9004×10
2.	$SO_2 = S + O_2$	1.3672×10^{-10}	4.1667×10^{-10}
3.	$SO_2 = SO + \frac{1}{2}O_2$	6.2632×10^{-6}	1.1617×10^{-5}
4.	$\underline{C} + SO_2 = CO + \frac{1}{2}O_2$	2.5351×10^{-1}	4.3496×10^{-1}
5.	$\underline{C} + O_2 = 2CO$	1.4488×10^{10}	9.2673×10^{10}

$$\therefore p^3S_2 = \frac{K_2 \times p^2SO_2^3}{pO_2^2}$$

$$pS = \frac{K_2 \times pSO_2}{pO_2}$$

$$pSO = \frac{K_3 \times pSO_2}{\sqrt{pO_2}}$$

$$pCOS = \frac{K_4 \times a_C \times pSO_2}{\sqrt{pO_2}}$$

$$pCO = \sqrt{K_5 \times a_{CO} \times pO_2}$$

In which pSO_2 is the equilibrium value.

As a first approximation, it is assumed that the reaction

$$SO_2 + 2C = 2CO + \tfrac{1}{2}S_2$$

is completely to the right. This means that for every volume of SO_2 used, two volumes of CO are produced, and we may assume that p CO is double the initial pSO_2.

By using this approximate value of CO, and the calculated value of a_C and the K value for the reaction

$$2C + O_2 = 2CO$$

an approximate value of pO_2 is calculated.

The value of pO_2 (approx) is now used for calculation of the partial pressures of the reacting gas species, substituting X as the equilibrium value of pSO_2, so that at 1400°C.-

$$pS_2 = \frac{1{\cdot}0975 \times 10^{-6{\cdot}6} \times X^3}{pO_2^2}$$

$$pS = \frac{1.3672 \times 10^{-10} \times X}{pO_2}$$

$$pSO = \frac{6.2632 \times 10^{-9} \times X}{\sqrt{pO_2}}$$

$$p\,COS = \frac{2.5351 \times 10^{-4} \times a_C \times X}{\sqrt{pO_2}}$$

so that the values of

$p\,S_2$ will be in the form $a\ X^3$

$p\ \ S$ " " " $b\ X$

$p\ \ SO$ " " " $c\ X$

$p\ \ COS$ " " " $d\ X$

Since for the formation of S_2 two parts of SO_2 are dissociated and for the formation of each of S, SO, COS one part of SO_2 is dissociated , i.e. initial $p\,SO_2 = 2S_2 + SO + S + COS$

$$= 2a\ X^3 + (b + c + d)\ X$$

The above equation will be solved for the value X, which will be the equilibrium value of SO_2. Now since the total O_2 comes from total SO_2

$$SO_2 = O_2 + S$$

so that total O_2 = initial SO_2 = $\frac{1}{2}SO + \frac{1}{2}CO + SO_2 + \frac{1}{2}COS + O_2$ (equilib)

$\therefore \frac{1}{2}pCO$ = initial SO_2 - $(\frac{1}{2}SO + \frac{1}{2}COS + SO_2 + O_2)$

from which the equilibrium $p\,CO$ is calculated. The calculated new value of $p\,CO$ is used in calculation of pO_2, and the whole procedure is repeated so many times until a constant value of the partial pressure of the reacting gas species is obtained.

In the case where the gas phase was a mixture of SO_2, CO_2 and argon, the reactions which may occur between the gas phase and the melt would be the same as in the case of SO_2 but with the addition of the reaction

	$K_{1673}\,^{\circ}K$	$K_{1723}\,^{\circ}K$
$CO_2 + C = 2CO$	$6{\cdot}116 \times 10^{3}$	$9{\cdot}0261 \times 10^{3}$

In this case, it is assumed as a first approximation that both the reactions

$$SO_2 + 2\underline{C} = 2CO + S$$

$$CO_2 + \underline{C} = 2CO$$

are complete so that the approximate value of $pCO = 2pSO_2$ (initial) + $2pCO_2$ (initial).

From this value is calculated the approximate equilibrium value of pCO_2

e.g. at 1400°C $\quad pCO_2 = \dfrac{pCO^2}{6{\cdot}116 \times 10^3 \times a_{\underline{C}}}$

The approximate values of pS_2, pS, pSO, $pCOS$, pO_2 and pSO_2 are calculated using the same procedure applied in the case of SO_2 alone. In this case since the total oxygen comes from total SO_2 + total CO_2

$\therefore$ total O_2 = initial pCO_2 + initial pSO_2

$= pO_2 + pSO_2 + pCO_2 + \frac{1}{2}pSO + \frac{1}{2}pCOS + \frac{1}{2}pCO$

i.e. $\frac{1}{2}pCO_{equil}$ = (initial CO_2 + initial SO_2) − (PO_2 + pSO_2 + pCO + $\frac{1}{2}pSO$ + $\frac{1}{2}pCOS$)

the equilibrium new value of pCO is calculated from which is calculated the new equilibrium values of pCO_2 pSO_2 and the whole procedure is repeated till constant values of the partial pressure of the gases are obtained.

Calculation of the Sulphur and Oxygen Fluxes.

These calculations are based on experimental observations discussed later leading to the assumption that the sulphur pick up by the metal is according to a temporary steady state condition.

$$J_S = \frac{D_S \left(C_S^e - Cb^S \right)}{L}$$

$$J_O = \frac{D_O \left(C_S^e - Cb^O \right)}{L}$$

where J_S = sulphur flux

D_S = diffusion coefficient of sulphur in liquid iron ($= 3 \times 10^{-5}$ at 1400° - 1450°C range)[98]

C_S^e = the equilibrium value of % S on the surface of the melt.

C_b^S = the bulk concentration of sulphur (estimated by analysis)

J_O = the oxygen flux

D_O = diffusion coefficient of oxygen in liquid iron ($= 5 \times 10^{-5}$ at 1400 - 1450°C range)[99]

C_S^e = the equilibrium value of % O on the surface of the melt.

Cb^O = the bulk concentration of oxygen (zero in case of carbon saturated iron).

L = is the thickness of the melt.

The sulphur equilibrium surface concentration was calculated as follows.

The standard free energy of solution of gaseous sulphur in liquid iron is given by Sherman, Elvander and Chipman[12] as

$S_2 = 2\underline{S}_{1\ wt\%}$

$$\Delta G^\circ = -63,040 + 10{\cdot}54\ T$$

using the pS_2 and the K value for the above reaction at the experimental temperature

$$a\underline{S} = \sqrt{K \times pS_2}$$

$\log f_S^C$ and in the case of the Fe-C-Si alloys

the $\log f_S^X = \log f_S^C + \log f_S^{Si}$ is calculated using the graphical method given by Sherman and Chipman[20].

Thus $\%S$ at surface $= \dfrac{a\,\underline{S}}{f_S}$

$$\therefore \quad C_S^S = \frac{\%S \times \text{density of liquid iron}}{100 \times \text{molecular wt S.}} = \text{moles/cm}^3$$

The equilibrium $\underline{O}$ surface concentration was calculated as follows.

The free energy of solution of gaseous oxygen in liquid iron

$$\tfrac{1}{2} O_2 = \underline{O}_{1\ wt\ \%}$$

was given by Chipman et al[34] as

$$\Delta G^\circ = -28,220 + 0{\cdot}57\ T$$

Using pO_2 and the K value for the above reaction at the experimental temperature

$$\Delta\,\underline{O} = K \sqrt{pO_2}$$

using the value of $\log f_O = -0{\cdot}421 \times \%\,\underline{O}$ given by Sawamura and

$$\therefore \quad \%\,O_2 \text{ wt } \% \quad \text{at metal surface} = \frac{a\,Q}{f_O}$$

$$C_g^O = \frac{\%\,O \times \text{density of liquid iron}}{100 \times \text{molecular wt oxygen}} = \text{moles/cm}^3$$

Calculation of the Actual Rate of Sulphur Pick Up

This was obtained by dividing the experimental results of the amount of sulphur picked up in grams/minute over the surface area of the melt x 60 to give the rate in grams/cm^2/second. An accurate value for the actual rate of carbon loss could not be evaluated due to experimental difficulties.

It was assumed that the rate of carbon loss will follow the same course as the rate of S pick up so that from the total values of S pick up and C loss and the experimental value of S pick up/ minute, a relative value of carbon lost in grams/minute was calculated, from which a provisional figure for the actual rate of carbon loss was given. It is to be stressed here that this figure is only very approximate.

TABLE I

Experiment	Temp. °C	Gas Mixture Argon +	Alloying elements %	e_0	p CO $\times 10^{-3}$	p S_2 $\times 10^{-4}$	p S $\times 10^{-6}$	p COS $\times 10^{-6}$	p CO_2 $\times 10^{-8}$	p SO $\times 10^{-10}$	p SO_2 $\times 10^{-15}$	p O_2 $\times 10^{-21}$
1	1400	0·1% SO_2	4% C	0·3933	1·9997	4·562	0·6835	2·718	-	1·707	1·15	1·7796
2	"	0·17% "	"	0·4126	3·474	8·167	1·175	6·3	-	3·77	4·22	4·91
3	"	0·457% "	"	0·3623	9·126	21·75	1·925	27·08	-	18·45	61·64	43·78
4	"	0·66% "	"	0·4288	13·17	31·66	2·322	47·11	-	27·14	110·6	65·12
9	1450	0·1% "	"	0·473	1·9997	4·372	1·245	2·68	-	1·516	0·57	1·908
10	"	0·17% "	"	0·473	3·4737	7·838	1·667	6·24	-	3·525	2·303	5·758
11	"	0·457% "	"	0·450	9·12	21·34	2·75	27·07	-	16·067	28·98	43·9
12	"	0·66% "	"	0·473	13·172	31·15	3·324	47·26	-	26·53	65·4	82·02
5	1400	0·1% "	"	0·3713	1·997	4·572	0·683	2·71	-	1·953	1·55	2·402
6	"	0·17% "	"	0·7126	3·474	8·107	1·173	6·3	-	3·772	4·22	4·91
7	"	0·457% "	"	0·7989	9·126	21·76	1·925	27·127	-	13·43	32·53	23·09
8	"	0·66% "	"	0·7989	13·173	31·66	2·322	47·12	-	23·33	81·72	48·11

TABLE I -(CONTINUED)

Experiment	Temp. °C	Gas Mixture Argon +	Alloying elements %	a_C	p CO x 10^{-3}	p S_2 x 10^{-4}	p S x 10^{-4}	p COS x 10^{-6}	p CO_2 x 10^{-8}	p SO x 10^{-10}	p SO_2 x 10^{-15}	p O_2 x 10^{-2}
13	1450	0·1% SO_2	4% C	0·4501	1·9973	4·367	1·247	2·689	-	1·447	0·638	2·13
14	"	0·17% "	"	0·4501	3·474	7·864	1·67	6·256	-	3·735	2·58	6·44
16	"	0·457% "	"	0·3733	9·129	21·367	2·753	27·686	-	18·947	40·28	60·99
15	"	0·66% "	"	0·4501	13·173	31·158	3·324	47·2	-	28·01	72·91	91·43
18	1400	0·1% "	4·27%C.	0·5156	1·9997	4·568	0·682	2·717	-	1·302	0·67	1·0384
17	"	0·17% "	"	0·4513	3·474	8·09	1·1737	6·279	-	3·438	3·51	4·068
19	"	0·457% "	"	0·4146	9·126	21·76	1·925	27·06	-	14·31	37·02	26·33
20	"	0·66% "	"	0·4513	13·173	31·65	2·32	47·11	-	25·79	99·85	56·8
21	1450°	0·1% "	"	0·5132	1·9997	4·388	1·247	2·689	-	1·399	0·485	1·621
22	"	0·17%	"	0·4501	3·474	7·864	1·67	6·256	-	3·753	2·58	6·44
23	"	0·457%	"	0·4501	9·12	21·34	2·75	27·07	-	16·06	28·98	43·91
24	"	0·66%	"	0·5132	13·174	31·18	3·32	47·22	-	24·57	56·1	70·33

TABLE I - (CONTINUED)

Experiment	Temp. °C	Gas Mixture Argon +	Alloying elements %	a_C	p CO x 10^{-3}	p S_2 x 10^{-4}	p S x 10^{-4}	p COS x 10^{-6}	p CO_2 x 10^{-6}	p SO x 10^{-10}	p SO_2 x 10^{-15}	p O_2 x 10^{-2}
25	1400	0·66%SO_2	4·27%C 1·83%Si	1	13·172	31·75	2·302	47·0	-	11·7	19·7	11·7
26	"	0·17%"	4·27%C 1·83%Si	1	3·474	7·818	1·154	6·176	-	1·526	0·703	0·83
27	"	0·66% "	4·27°C 0·73%Si	1	13·172	31·75	2·302	47·0	-	11·4	19·7	11·7
28	"	0·17% "	4·27%C 0·73%Si	1	3·474	7·818	1·154	6·176	-	1·526	0·703	0·83
29	"	0·66% "	4·27%C 5·6%Si	1	13·177	31·75	2·302	47·0	-	11·4	19·7	11·7
30	"	0·17% "	4·27%C 5·6%Si	1	3·474	7·818	1·154	6·176	-	1·526	0·703	0·83
31	"	0·66% "	4·27%C	1	13·172	31·75	2·302	47·0	-	11·4	19·7	11·7
32	"	0·17% "	4·27%C	1	3·474	7·818	1·154	6·176	-	1·526	0·703	0·83
33	"	0·66% "	4·27%C	1	13·172	31·75	2·302	47·0	-	11·4	19·7	11·7

TABLE I - (CONTINUED)

Experiment	Temp. °C	Gas Mixture Argon +	Alloying elements %	a_C	p_{CO} x 10^{-3}	p_{S_2} x 10^{-4}	p_S x 10^{-4}	p_{CS} x 10^{-6}	p_{CO_2} x 10^{-6}	p_{SO} x 10^{-10}	p_{SO_2} x 10^{-15}	p_{O_2} x 10^{-2}
34	1400	0.66%SO_2	4.27%	1	13.172	31.75	2.302	47.0	-	11.4	19.7	11.7
35	"	0.17% "	"	1	3.474	7.818	1.154	6.176	-	1.526	0.703	0.83
36	"	0.17% "	"	1	3.474	7.818	1.154	6.176	-	1.526	0.703	0.83
38	"	0.66%SO_2 0.1% CO_2	"	0.6257	15.17	31.63	2.321	54.25	6.014	21.42	68.9	40.58
40	"	0.66%SO_2 1% CO_2	"	0.6257	33.17	31.3	2.309	117.99	28.74	46.59	327.6	194.0
41	"	0.66%SO_2 0.66%CO_2	"	0.6257	26.34	31.37	2.312	94.14	18.66	37.98	217.5	128.2
42	"	0.66%SO_2	2.97%C	0.2076	13.173	31.66	2.322	47.12	-	56.08	472.0	277.89
48	1459	"	2.97%C	0.2457	13.172	31.47	3.324	47.3	-	51.7	246.0	311.5
49	"	"	2%C	0.1038	13.172	31.16	3.324	47.3	-	123.2	1410.0	1761.6
50	"	0.66%SO_2 0.66%CO_2	4.27%C	0.45	26.34	30.98	3.315	94.3	17.19	56.3	295.4	371.5

TABLE I - (CONTINUED)

Experiment	Temp. °C	Gas Mixture Argon +	Alloying elements %	a_C	p CO $\times 10^{-3}$	p S_2 $\times 10^{-6}$	pS $\times 10^{-6}$	p COS $\times 10^{-6}$	p CO_2 $\times 10^{-6}$	p SO $\times 10^{-10}$	p SO_2 $\times 10^{-15}$	p O_2 $\times 10^{-3}$
53	1400	0·66%SO_2	4·27%C	0·4746	13·173	31·67	2·322	47·24	-	24·98	93·54	55·05
54	"	"	2·97%C	0·2437	13·173	31·665	2·322	47·21	"	47·74	342·1	201·4
55	1450	"	4·27%C	0·473	13·172	31·153	3·324	47·26	-	26·53	65·4	82·02
56	"	"	2·97%C	0·2319	13·173	31·166	3·324	47·2	-	54·36	274·6	344·3
57	1450	0·66%SO_2 0·66%CO_2	4·27%C	0·2457	26·34	30·93	3·312	94·04	31·3	102·2	974·6	1226·8
58	1400	"	4·27%C	0·4746	26·34	31·33	2·31	115·68	23·9	59·88	541·0	320·2

TABLE II

Experiment	Temp. C°	Gas Mixture Argon +	Wt. of Sample (gm)	Surface Area (cm^2)	Depth of Sample (cm)	Amount of S pick up gm/min/gm $\times 10^{-5}$	Actual rate of S pick up gm/cm/sec $\times 10^{-5}$	J_s gm/cm^2/sec $\times 10^{-5}$	J_o gm/cm^2/sec $\times 10^{-5}$	Estimated rate of carbon loss gm/cm^2 sec $\times 10^{-5}$	Remarks
1	1400	0.1%SO_2	20	5	0.7	3	0.333	2.45	0.30	2.2	
2	"	0.17% "	"	"	"	11	0.733	3.14	0.556	3.6	
3	"	0.457% "	"	"	"	35	2.33	5.46	1.37	6.3	
4	"	0.66% "	"	"	"	50	3.33	6.07	2.1	4.7	
9	1450	0.1% "	"	"	"	5	0.2	1.6	0.362	6.5	
10	"	0.17% "	"	"	"	14	0.933	2.37	0.63	4.8	
11	"	0.457% "	"	"	"	45	3	3.66	1.58	5.1	
12	"	0.66% "	"	"	"	68	5.67	4.27	2.37	6	
5	1400	0.1%	10	3	0.6	6	0.44	3.02	0.34	8	
6	"	0.176%	"	"	"	8	0.44	3.67	0.65	6.5	
7	"	0.457% "	"	"	"	24	1.33	6.53	1.68	3	
8	"	0.66%	"	"	"	50	3.33	6.6	2.72	4	

TABLE II - (CONTINUED)

Experiment	Temp. °C	Gas Mixture Argon +	Wt. of Sample (gm)	Surface Area (cm^2)	Depth of Sample (cm)	Amount of S pick up gm/min/gm $\times 10^{5}$	Actual rate of S pick up $gm/cm^2/sec \times 10^{-5}$	J_D $gm/cm^2/sec \times 10^{-6}$	J_O $gm/cm^2/sec \times 10^{-4.0}$	Estimated rate of carbon loss $gm/cm^2/sec \times 10^{-5}$	Remarks
13	1450	0.1%SO_2	10	3	0.6	7	0.4	1.1	0.406	3	
14	"	0.17% "	"	"	"	17	0.94	2.59	0.705	6	
16	"	0.457% "	"	"	"	39	2.166	4.68	1.62	0	
15	"	0.66% "	"	"	"	65	3.61	5.16	2.65	4	
18	1400	0.1% "	5	2.2	0.4	9	3.41	3.54	0.63	5	
17	"	0.17% "	"	"	"	9	3.41	5.25	0.98	5	
19	"	0.437% "	"	"	"	102	3.86	8.5	2.74	5	
20	"	0.66% "	"	"	"	135	5.1	10.39	3.75	6	
21	1450	0.1% "	"	"	"	25	0.94	2.59	0.66	5.5	
22	"	0.17% "	"	"	"	25	0.94	3.68	1.05	6.2	
23	"	0.457% "	"	"	"	120	4.54	6.39	2.76	5.3	
24	"	0.66% "	"	"	"	176	6.66	6.897	4.35	5.6	

TABLE II - (CONTINUED)

Experiment	Temp. °C	Gas Mixture Argon +	Wt. of Sample (gm)	Surface Area (cm^2)	Depth of Sample (cm)	Amount of S pick up gm/min /gm $\times 10^{-5}$	Actual rate of S pick up gm/cm^2 /sec $\times 10^{-8}$	J_D gm/cm^2 /sec $\times 10^{-5}$	J_O gm/cm^2 /sec $\times 10^{-10}$	Estimated rate of carbon loss gm/cm^2 sec $\times 10^{-5}$	Remarks
25	1400	0.66 CH_4	10	3	0.6	62	3.44	4.58	1.21	3.6	3.83% Si
26	"	0.176% "	"	"	"	21	1.27	1.6	0.512	3.2	"
27	"	0.66% "	"	"	"	56	2.777	4.91	1.94	2.7	0.73% Si
28	"	0.17% "	"	"	"	18	1	2.38	0.503	2.6	"
29	"	0.66% "	"	"	"	70	3.89	1.15	1.21	8.8	5.6% Si
30	"	0.17% "	"	"	"	24	1.166	8.59	0.324	7.9	"
31	"	0.66% "	"	"	"	70 +	3.89	3.9	4.3	-	carbon boat
32	"	0.17% "	"	"	"	22 +	1.22	2.4	0.77	-	"
33	"	0.66% "	"	"	"	70 +	3.89	5.2	2.2	1.6	graphite shield
34	"	0.66% "	"	"	"	70 +	3.89	3.9	4.3	-	graphite powder added
35	"	0.17% "	"	"	"	22 +	1.22	2.6	0.59	1.6	graphite shield
36	"	0.17% "	"	"	"	22 +	1.22	2.4	0.77	-	graphite powder added

+ Value is estimated

TABLE II - (CONTINUED)

Experiment	Temp. °C.	Gas Mixture Argon +	Wt. of Sample (gm)	Surface Area (cm^2)	Depth of Sample (cm)	Amount of S pick up gm/min /gm	Actual rate of S pick up gm/cm^2 /sec	J_s gm/cm^2 /sec	J_o gm/cm^2 /sec	Estimated rate of carbon loss gm/cm^2 /sec	Remarks
					$\times 10^{3}$	$\times 10^{-5}$	$\times 10^{-3}$	$\times 10^{-6}$	$\times 10^{-10}$	$\times 10^{-5}$	
38	1400	0.66% SO_2 0.1% CO_2	10	3	0.6	52	2.69	5.5	3.5	2.4	
40	"	0.66% SO_2 1% CO_2	"	"	"	38	2	5.6	7.8	4	
41	"	0.66% SO_2 0.66% CO_2	"	"	"	42	2.22	5.59	6.36	3.7	
42	"	0.66% SO_2	"	"	"	25	1.388	9.78	1.94	7.5	
48	1450	0.66% SO_2	"	"	"	56	3.16	6.75	2.05	4.3	
49	"	0.66% "	"	"	"	54	3	5.15	1.85	4.3	
50	"	0.66% SO_2 0.66% CO_2	"	"	"	59	3.22	5.14	5.35	4.6	
53	1400	0.66% SO_2	20	4	0.9	53	4.4	4.55	1.76	11.2	
54	"	0.66% SO_2	"	"	"	48	4	6.2	0.13		
55	1450	0.66% SO_2	"	"	"	60	5	3.3	1.85	12.7	
56	"	0.66% SO_2	"	"	"	50	4.16	4.7	1.34	6.9	
57	"	0.66% SO_2 0.66% CO_2	"	"	"	53	4.6	4.45	2.7	5.6	
58	1400	0.66% SO_2 0.66% CO_2	"	"	"	50	4.16	4.54	4.24	11.0	

D I S C U S S I O N

DISCUSSION

The results of this work are considered to justify

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1. That there is local equilibrium between the melt and the gas film immediately adjacent to it.
2. That the overall reaction for the sulphur pick up by the metal is

$$SO_2 + 2\underline{C} = 2\,CO + \underline{S}$$

which may be written as

$$SO_2 = \underline{S} + O_2$$

$$O_2 + 2\underline{C} = 2\,CO$$

The most important single observation in this work has been the behaviour characterising the sulphur pick up by the melt. This was the fact that in every experiment, the amount of pick up decreased with time till a stage was reached at which the amount of pick up became constant. It has been deduced from this behaviour that sulphur is picked up at the surface of the metal, till a sulphur rich layer is formed. After the formation of this layer the amount of pick up became constant and was governed by the rate of diffusion of sulphur from this layer at the surface of the metal to the bulk of the melt.

The variations of this behaviour under different experimental conditions do conform with this view. It has been observed that at

higher temperature , more time was taken till the steady pick up stage was reached. This could be explained on the basis that at higher temperature the sulphur transport rate would be higher and the stirring conditions would be better, so that more time would be taken for the formation of a sulphur layer. It has been also observed that, in experiments, where higher sulphur potential in the gas phase was used, the time taken to reach the steady pick up stage was much shorter than that observed when using a gas with low sulphur potential. Obviously, the higher the sulphur potential of the gas in contact with the melt, the quicker will be the equilibration of the melt surface with the sulphur in the gas.

Although no quantitative relation could be given to describe this behaviour, it could be argued that once this sulphur layer is formed at the surface of the melt, and since the difference in concentration of sulphur between this layer and the bulk of the metal is very high, then, the sulphur pick up by the melt is governed by a semi, or temporary steady state condition under which the rate of sulphur pick up at the surface of the melt is equal to the rate of diffusion of sulphur from the surface to the bulk of the melt. Thus we would be entitled to the use of Fick's second law in the interpretation of the results of this work.

The effects of variation of p SO_2 and of the melts surface area on the amount of pick up is straightforward and is to be expected in a mass transfer process. Here the greater the difference in concentration of sulphur between the gas phase and the melt, and the greater the contact area between the two phases, the greater will be the transfer of sulphur. This is in general accordance with the results of this work.

The effect of the carbon content of the metal on the amount of pick up is very intriguing. Carbon increases the activity coefficient of sulphur in liquid iron, and as such, the higher the carbon content, the lower the amount of pick up one would expect. The results of this work show the opposite tendency. This tendency can be explained, if we consider melt as being in equilibrium with the gas film immediately adjacent to it. Thus, the partial pressures of the gas species in the gas film in contact with the melt will be fixed by the carbon content of the melt. A look at Table I will show that the effect of carbon activity on the p S_2 is not very great. Most important is the effect of activity of carbon on the PO_2. Table I shows that for an experiment where $a_C = 1$, and for a gas mixture containing 0·66% SO_2, p S_2 is $3{\cdot}175 \times 10^{-9}$ and p O_2 is $1{\cdot}17 \times 10^{-20}$. For a sample where $a_C = 0{\cdot}21$ and for a gas mixture containing 0·66 % SO_2, p $S_2 = 3{\cdot}166 \times 10^{-9}$ and p $O_2 = 2{\cdot}6 \times 10^{-19}$ for a sample where $a_C = 0{\cdot}625$ and where the gas mixture 0·66 % SO_2 and 0·66 % CO_2, the p $S_2 = 3{\cdot}137 \times 10^{-9}$ and p $O_2 = 1{\cdot}28 \times 10^{-19}$. It could be seen that the effect of change

in a_C on the change in pS_2 is not important compared with the effect on the change in pO_2. Decreasing the a_C from 1 to 0·2 increases pO_2 in the gas film twenty times. Addition of the same amount of CO_2 as SO_2 to the gas phase only increases pO_2 about ten times. Now, if we consider the reactions

$$SO_2 = S + O_2$$

$$O_2 + 2C = 2CO$$

it will be apparent that by decreasing the pO_2, we are promoting the sulphur solution in the metal, so that the higher the a_C, the lower pO_2, the higher the amount of pick up. From the above discussion it could be argued that since the effect of decreasing a_C in the melt from 1 to 0·2 on increasing pO_2 is greater than the addition of the same volume of CO_2 to SO_2, then the amount of sulphur pick up for the sample where $a_C = 0·2$ must be lower than in the experiment where $a_C = 1$. and lower also than in the experiment where CO_2 was added. This is exactly what happened and the results of experiments B, 41 and 42 in Fig. 30 confirm this tendency.

On this basis also the results of the experiments where silicon was added to the melt may be explained. It looks as if the effect of silicon as a graphitiser overrides its other effects in our case. Here the graphite would lower pO_2 and this results in more sulphur pick up.

The effect of temperature on amount of pick up is less clear, although at higher temperature, the pO_2 was greater than pO_2 at lower temperature for the same pSO_2, which should result in a lower pick up at higher temperatures. The results of this work show the opposite tendency. Although the diffusion coefficient of sulphur is higher at higher temperature, the difference is however not enough to explain the higher amount of pick up at higher temperature. The explanation could be that at higher temperature, more efficient stirring is available resulting in an improved rate of sulphur transfer. This might explain the fact that at higher temperatures, the comparative effects of change in carbon content of sample, addition of silicon to the alloy, and the addition of CO_2 to the gas is not as clear or pronounced as the case at lower temperatures.

Table II is a summary of the results of this work, in which the actual rate of sulphur pick up is compared with the theoretical sulphur flux and oxygen flux. (In the calculation of Js and Jo local equilibrium has been assumed). Although there is no clear cut agreement between individual data, it is quite apparent that the actual rate of sulphur pick up has the same magnitude as the sulphur flux. This could only mean, that under the experimental conditions under which this work has been done, the rate controlling process

in the sulphur pick up by the liquid iron was the diffusion of sulphur from the surface of the metal to its bulk. This is not surprising in a case as this where artificial stirring is absent, and where the pick up is independent of flow rate so that the possibility of control of the process by sulphur transfer from the gas phase to the gas/metal boundary layer is excluded.

Although the data for the rate of carbon loss are only estimated, they however have the same magnitude as the rate of sulphur pick up.

APPLICATION TO OPEN HEARTH STEELMAKING

The results of this work are considered applicable to the melting down stage in the open hearth furnace. At this stage the slag has not yet formed and the gases and metal are in direct contact. The over-riding effects of the rate of combustion of the furnace gases and of its oxidising potential have been very early recognised. Dewing and Richardson[25] in considering the mechanism of pick up of sulphur by the charge from the furnace gases during melting in the open hearth assumed that the extent of sulphur pick up is governed by the amount of sulphur absorped by a film or layer of oxide which is almost certainly covering the metal during its melting. In their estimation of the amount of sulphur absorbed in this way, they assume that the Fe_2O_3/FeO ratio in the melting oxide drippings reflects the CO_2/CO ratio in the furnace atmosphere, i.e. when the melting oxides come to equilibrium with the gases. These authors considered it worth while to calculate the sulphur contents of the molten iron oxides which would be in equilibrium with gases of various CO_2/CO ratios resulting from the combustion of 1·2% S oil. Their results shown at Fig. 16 reflects the marked decrease in danger of sulphur pick up with the increasing degree of combustion of the gases.

The results of this work are considered to reflect the prime importance of the gas oxygen potential in equilibrium with the melt. It is considered more likely that the gases come to equilibrium with the melt and that in calculation of the oxidising potential of the furnace gases the effects of the melt on the partial pressure of gases must be taken care of. It is considered that the reactions

$$Fe + \tfrac{1}{2}O_2 = FeO \quad \text{and} \quad \underline{C} + \tfrac{1}{2}O_2 = CO$$

which may be written as

$$CO_2 + Fe = FeO + CO \quad \text{and} \quad CO_2 + \underline{C} = 2CO$$

are very important in the determination of the oxygen potential in contact with the metal, which governs the extent of sulphur pick up. It appears thus that the pO_2 in contact with the metal is lower than that of the furnace atmosphere, so that the extent of sulphur pick up must be higher than that calculated by Loving and Richardson. While these authors contended that the lower oxygen potentials at the Fe/FeO interface do not appear to be controlling, otherwise much greater absorption would have occurred in their experiments, Alwan and Bills[20] working at a constant CO_2/CO

ratio, found that both the rate and amount of sulphur transfer to slags depended on the state of oxidation of the slag. They also pointed out that in considering the reaction

$$\tfrac{1}{2}S_2 + \overline{O}^{--} = \overline{S}^{--} + \tfrac{1}{2}O_2$$

higher sulphur concentration than the equilibrium values were obtained. This last point was also found by St. Pierre and Chipman[33]. Earnshaw[11] pointed out that the absorption of sulphur by molten Fe-C alloys from the gas phase could not take place without a simultaneous absorption of oxygen by the metal and hence the removal of carbon. He found out that the change in rate of carbon removal was almost proportional to the change of sulphur pick up. In fact this has been confirmed in this work. The rate of carbon loss was found to have the same magnitude as the rate of sulphur pick up.

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A C K N O W L E D G E M E N T S

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APPENDIX

APPENDIX

ANALYSIS OF THE SAMPLES FOR SULPHUR

The number of runs carried out differed from one experiment to the other (Chapter 4). The value of sulphur content, given below, should not thus be taken as an indication of rate of sulphur pick up. From the number of runs carried out in each experiment, and from the value of pick up in each run, the sulphur content at the end of each experiment was calculated, and is compared with the analysed sulphur value.

Run	Estimated Sulphur gm	Analysed sulphur gm	Run	Estimated Sulphur gm	Analysed Sulphur gm
1	0.016	0.012	26	0.02	0.019
2	0.0385	0.0385	27	0.054	0.054
3	0.052	0.051	28	0.026	0.023
4	0.05	0.047	29	0.064	0.063
9	0.007	0.007	30	0.024	0.021
10	0.0165	0.016	31	0.52	0.068
11	0.052	0.049	32	0.14	0.09
12	0.0646	0.062	33	0.32	0.0663
5	0.009	0.00897	34	0.069	0.069
6	0.016	0.0137	35	0.073	0.028

Run	Estimated Sulphur gm	Analysed Sulphur gm	Run	Estimated Sulphur gm	Analysed Sulphur gm
7	0.036	0.036	36	0.03	0.031
8	0.026	0.0256	38	0.035	0.036
13	0.0056	0.005	40	0.04	0.04
14	0.0092	0.0088	41	0.031	0.0307
16	0.0347	0.034	42	0.03	0.028
15	0.0466	0.0456	46	0.058	0.0458
10	0.0046	0.0076	79	0.066	0.0643
17	0.0048	0.0038	50	0.066	0.063
19	0.053	0.051	53	0.096	0.089
20	0.073	0.073	54	0.087	0.082
21	0.009	0.009	55	0.097	0.095
22	0.011	0.01	56	0.094	0.092
23	0.0566	0.0525	57	0.097	0.093
24	0.0675	0.065	58	0.093	0.0917
25	0.0044	0.002			